THE GEOCHEMISTRY OF LOCH DUICH, SCOTLAND

by

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of the University of Edinburgh in the Faculty of Science.

1976

To

my

Parents

Declaration

This thesis has been composed by myself and describes laboratory and field work which I carried out.

Frontispiece: "the route which Johnson and Boswell followed, beautiful as it is, especially at its western end, where Loch Duich sleeps under the shadow of the five sisters of Kintail." (Blaikie, 1932)

A B S T R A C T

This study is concerned with the diagenetic reactions which occur within recent marine sediments and in particular with the speciation, associations and reactions of the trace metals (copper, zinc, iron and manganese) and organic matter in the sediments and their interstitial waters. For this purpose Loch Duich, a fjord type estuary on the N.W. coast of Scotland, is particularly suitable, since it has sediments of a vertically homogeneous lithology and grain size, contains sediments in various stages of reduction and is in an "unpolluted" region.

An integrated geochemical study of the sediments, interstitial waters and the overlying sea water was performed in which the grain size, mineralogy, major and trace element composition, organic carbon, total nitrogen and iodine measurements have been completed on the sediment. Temperature, salinity, dissolved oxygen, nutrients, and dissolved organic carbon (DOC) and trace metals were analysed in the overlying sea water. In addition, the chemical composition of the suspended particulate matter has been examined in order to obtain information on the sediment input and the chemical processes which occur in the water column.

The pore waters have been analysed for HCO_3^-, PO_4^{3-}, SO_4^{2-} and S^{2-} in order to define the biogeochemical metabolic zones present. The observed changes in dissolved trace metals and dissolved organic matter (DOM) are then related to the metabolic zones. In particular the geochemistry of the oxic and the sulphate reducing zones are compared and contrasted.

The changes of concentration and nature of the DOM with depth were investigated. It was shown by calibration against DOC (measured by dry combustion) that light absorbance at 280 nm is an accurate and simple measure of the concentration of DOC in pore waters. DOC remains constant in the oxic cores and increases with depth in the anoxic cores, the increase being entirely in the high molecular weight (HMW) fraction (MW > 1000). This HMW fraction was investigated using UV and IR spectroscopy and found to be principally fulvic acids and "melanoidins" with a small fraction ($\sim$1%) of humic acid.

The concentrations of dissolved trace metals Mn, Fe, Cu and Zn were found to be greater than those in sea water by at least an order of magnitude. In order to investigate the speciation of these metals in the pore waters, subsamples were ultrafiltered to separate the pore waters into a low molecular weight (LMW) and a HMW fraction, both of which were analysed for trace metals and DOC. In addition, the pore waters were oxidised, then ultrafiltered and the changes in LMW, HMW and total trace metal concentration noted.

These studies demonstrate that Mn is present in the pore waters as labile inorganic complexes. By contrast, Fe, Cu and Zn show no systematic trend and in addition are present in higher concentrations than would be predicted from the solubility products of the metal sulphides. Evidence is presented to show that these metals are present as organic chelates.

Analysis of the trace metal composition of the sediment shows that there is a surface enrichment of Zn and Pb of up to 100% despite the fact that this area is one of the least polluted in Europe. The problem of whether this is a natural enrichment or if it reflects an

influx of pollutants has been considered. A series of possible diagenetic recycling mechanisms between the solid phase and the pore waters have been proposed to explain the observed distribution of the trace metals Zn and Pb, dissolved manganese and iodine.

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CHAPTER 1

INTRODUCTION

The geochemical study of recent sediments was undertaken in the past to understand the transformations involved in the formation of sedimentary rocks (Larsen and Chilingar, 1967) and in particular the formation of certain economically important sediments such as metaliferous black shales (Presley et al., 1972) and petroleum (Emery and Rittenberg, 1953). More recently the study of recent sedimentary diagenesis has been considered important in its own right for the understanding of chemical changes and processes in the marine environment, in particular the chemical changes which affect organic and inorganic detritus in the marine environment prior to sedimentation, and the diagenetic changes which occur in the top metre of the sediment where biological activity is at a maximum. Additionally the diagenetic changes which occur in oxic and anoxic sediments are compared and contrasted. For this study, Loch Duich, a fjord type estuary in the N.W. of Scotland was chosen and an integrated geochemical study of the sediments, interstitial waters and the overlying sea water was performed.

Changes in pore water geochemistry are a particularly sensitive measure of diagenetic reactions occurring within the sediment. Chemical changes in the major anions (S^{2-}, SO_4^{2-}, Cl^-, PO_4^{3-} and HCO_3^-), trace metals (Fe, Mn, Cu and Zn) and dissolved organic matter (DOM) in the sediment interstitial waters were investigated. The changes

are related to metabolic processes and to known or observed changes in the geochemistry of the sediment. These natural processes must be understood as completely as possible because it is thought that reactions between sediments, interstitial waters and the overlying sea water may be important in the control of the concentration of certain chemical species in sea water (Krauskopf, 1956; Price, 1973). It is also necessary to understand the natural system as fully as possible in order to recognise changes in the sediments and overlying sea water brought about by pollution. In this regard the study of the diagenesis of trace metals and organic matter is particularly important since excess quantities of trace metals in certain forms are toxic to marine life, while a superabundance of organic matter gives rise to eutrophic conditions.

Because the seawater/sediment system is so complex, it requires a broad multidisciplinary approach in order to recognise all the parameters which could affect these processes. Thus, in addition to a geochemical investigation of the sediments and their pore waters, a study of the hydrography of the water column, the geochemistry of the particulate matter and the physical, mineralogical and chemical nature of the inorganic and organic fractions of the sediment in the loch basin and its catchment area was performed. The result is a detailed study similar to that performed on Saanich Inlet (Nissenbaum et al., 1972; Presley et al., 1972 and Brown et al., 1972).

In particular this study concentrates on understanding the diagenesis of trace metals and organic matter in the interstitial waters of recent marine sediments and relating the results to metabolic processes occurring within the sediment. The speciation and thus

geochemistry of trace metals in the interstitial waters of reducing sediments was thought to be controlled by DOM (Brooks et al., 1968; Presley et al., 1972; Duchart et al., 1973). In this study possible trace metal - organic matter relationships were investigated both by direct correlations between trace metals and DOM and by physical and chemical separations of organic phases which were thought to be possible chelating agents. In addition, changes in the chemical and physical nature of the pore waters during diagenesis affecting DOM were examined. Sulphide and nutrients were measured both as potential complexing species and in order to define the biogeochemical zone (oxic, sulphate-reducing, methane-producing) within which different chemical changes are observed. By relating changes in trace metals and DOM to these metabolically induced biogeochemical zones, it is possible to compare the results here to those found elsewhere and to predict within certain limits the geochemistry of other coastal sediments and their pore waters.

Attempts are also made to relate the geochemistry of the pore waters to diagenetic changes in the sediment. In particular it has been suggested that recycling mechanisms in the top metre of the sediment may control the observed geochemistry of trace metals and iodine in the sediment (Price, 1973); recycling which involves the burial of these elements with the sediment, solution into the pore waters as a result of diagenetic reactions, upward diffusion and precipitation close to the sediment-water interface. Such processes are investigated in detail with the data obtained in this study. An understanding of such recycling mechanisms is of great importance in the study and measurement of the fluxes of toxic trace metals into

sedimentary basins.

Loch Duich is particularly suitable for a study on the natural processes of recent sedimentary diagenesis, since it is situated in one of the most sparsely populated regions of western Europe. There is no local source of pollution, and thus any anthropogenic disturbance is likely to be small. The organic rich sediments of Loch Duich can also be considered as representative of a coastal marine area and specifically a stratified estuary, regions which will become of increasing importance both in terms of pollution and as an area being exploited for its natural resources.

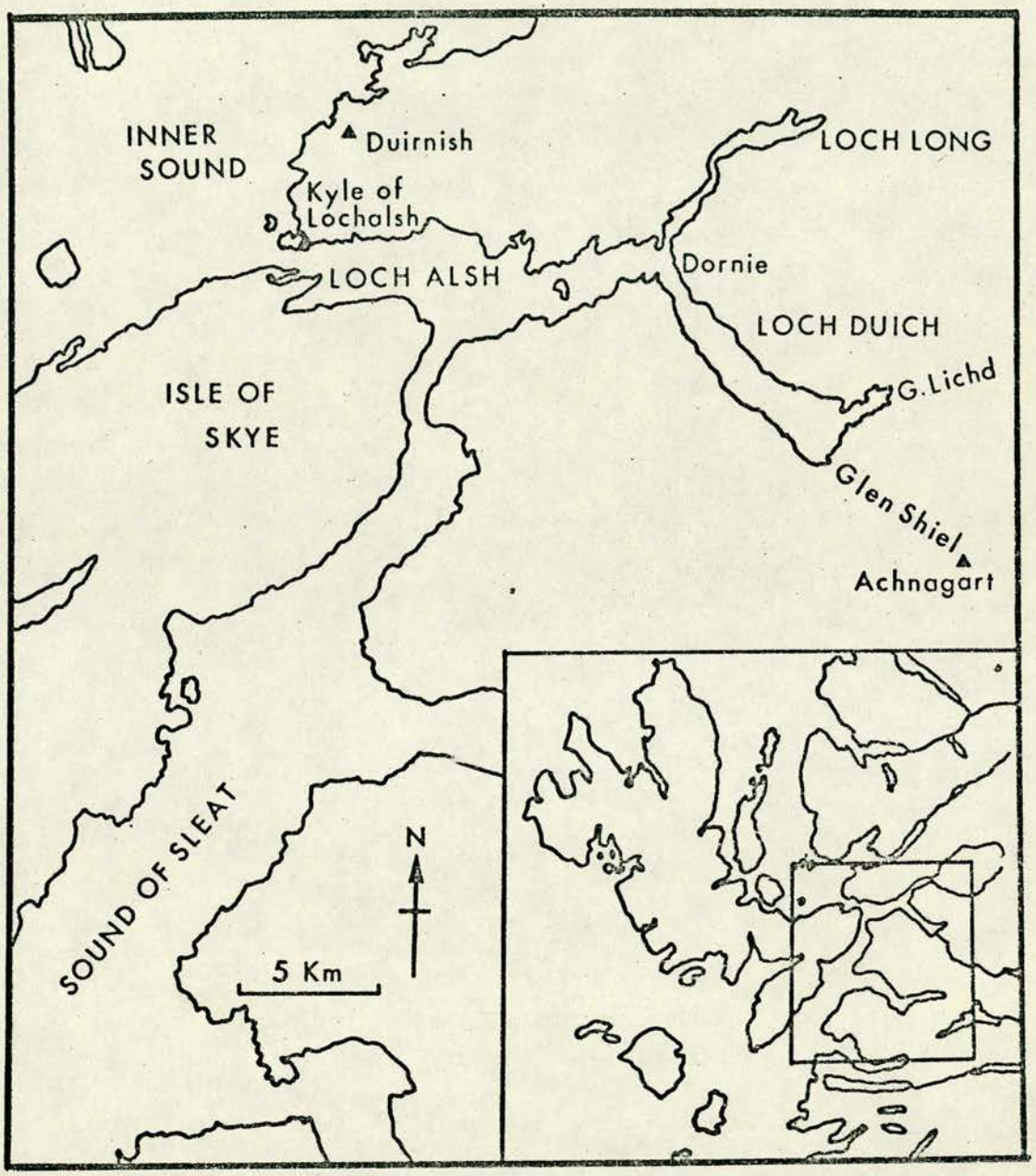


FIG 2.1; General Map of the Area of Loch Duich

CHAPTER 2

THE GEOLOGY AND GEOMORPHOLOGY OF THE LOCH DUICH AREA

2.1 Introduction to area

Loch Duich, the sea loch which was chosen for this study, is situated 64 miles from Fort William at the point where the "Road to the Isles", the A87 (Fort William - Kyle of Lochalsh road) reaches the sea (Fig. 2.1). The Loch is $7\frac{1}{2}$ km in length from Shiel Bridge at its head to its mouth between Dornie and Totaig, and 1 to $1\frac{1}{2}$ km wide. It is surrounded on all sides by hills of 2000 feet. To the south east rise the peaks of the five sisters of Kintail 3505 feet, the highest point within the region.

The Highlands of Scotland can be considered to be a deeply dissected plateau which slopes uniformly to the east (Peach and Horne, 1930). This results in relatively small catchment areas for the many sea lochs on the western coast of Scotland, of which Loch Duich is one; the catchment area is shown in Figure 2.2. The high elevation of the mountains in the path of moist, predominantly south westerly winds results in a very high annual rainfall, 150 inches on the Saddle and the five sisters of Kintail (Fig. 2.3). The rainfall is greatest during the winter months Nov - Feb, but there is no period in the year that is dry (Meteorological Office statistics) (Fig. 2.3). The high rainfall and small catchment area mean that the rivers are steep and fast flowing, and because of the basically impermeable nature of the underlying rock, the majority of the rainfall tends to find its way into the rivers and hence the sea lochs

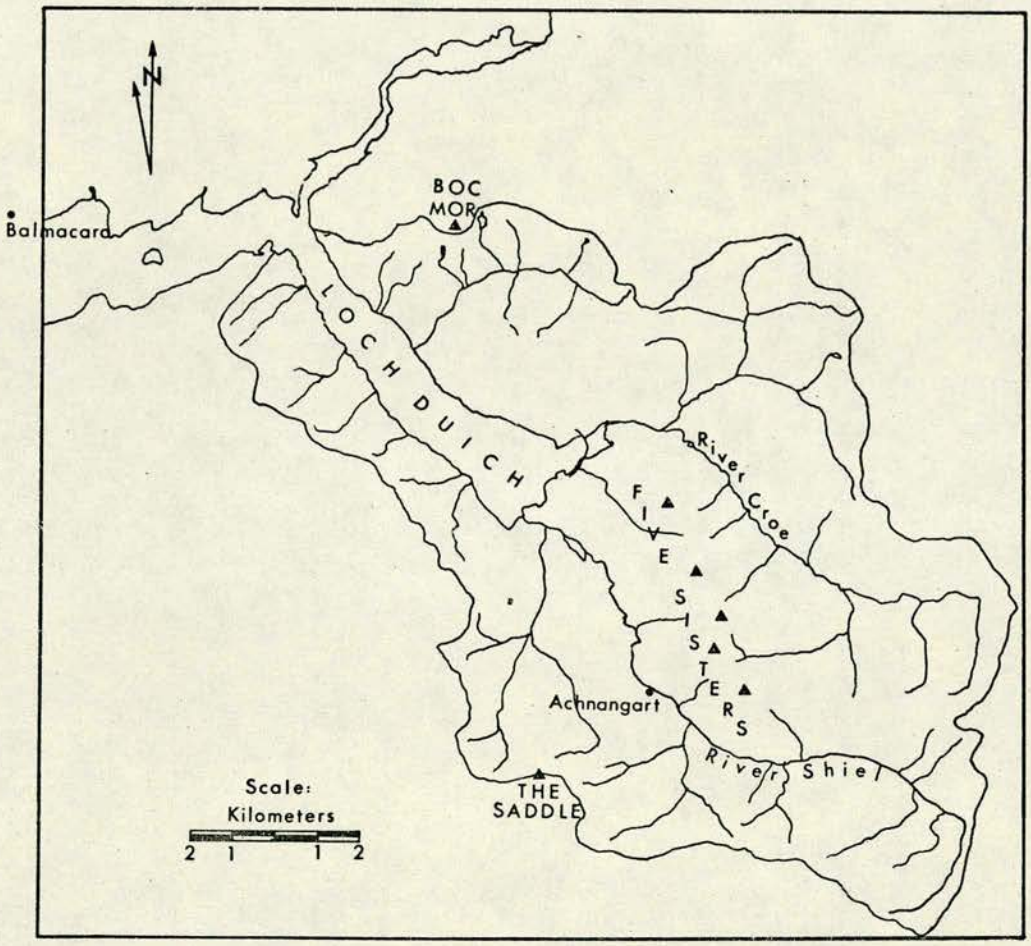


FIG. 2.2; Rainfall Catchment Area of Loch Duich

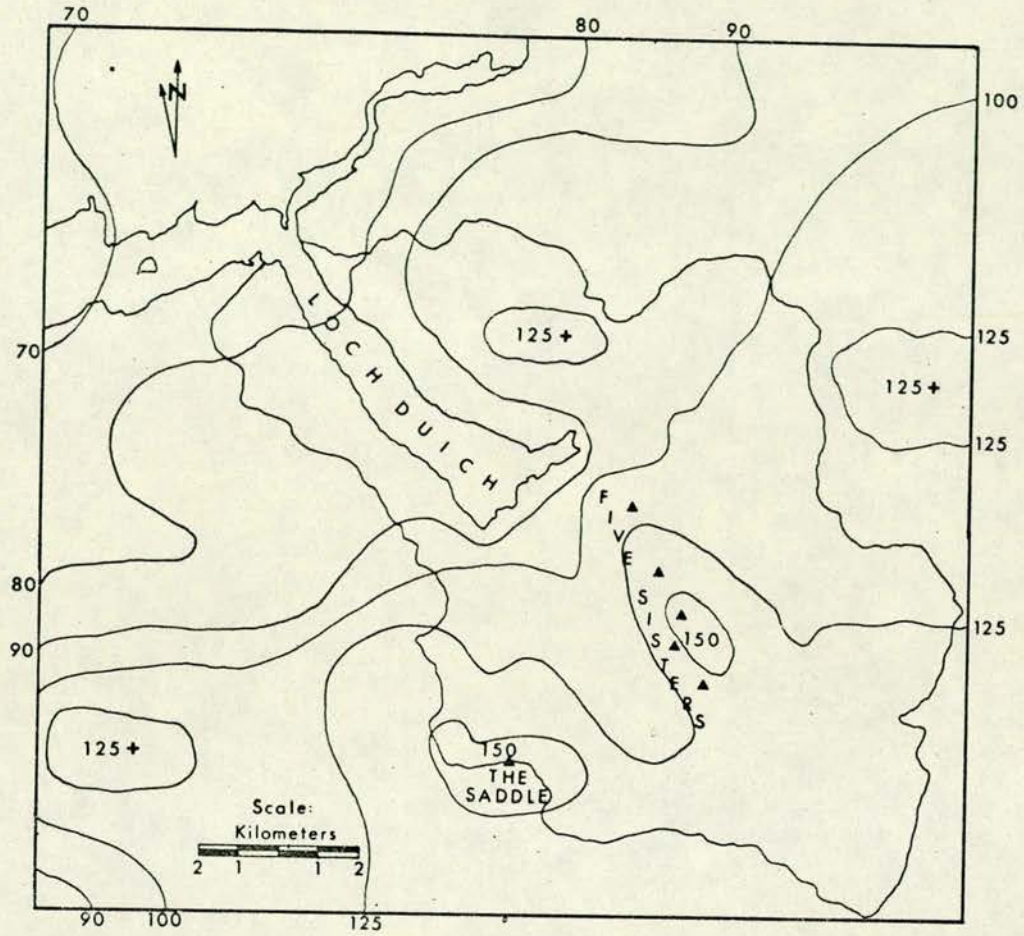
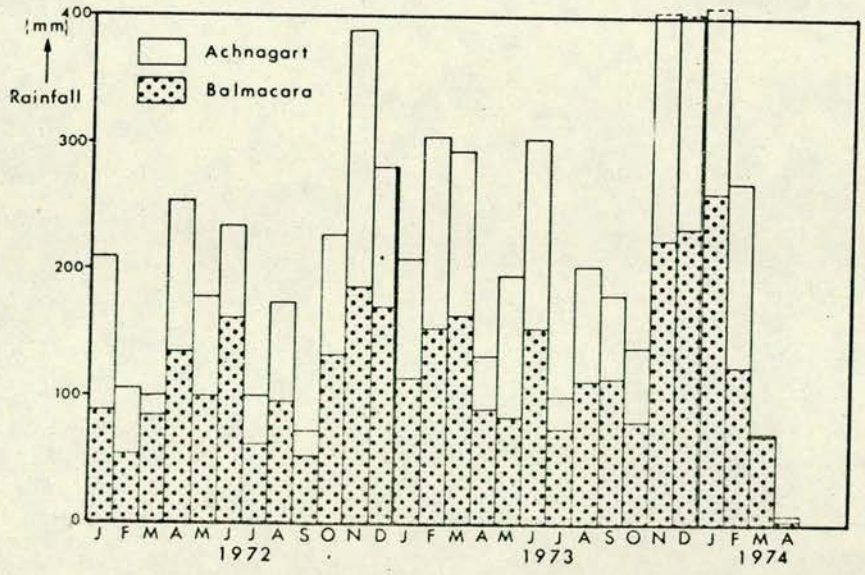


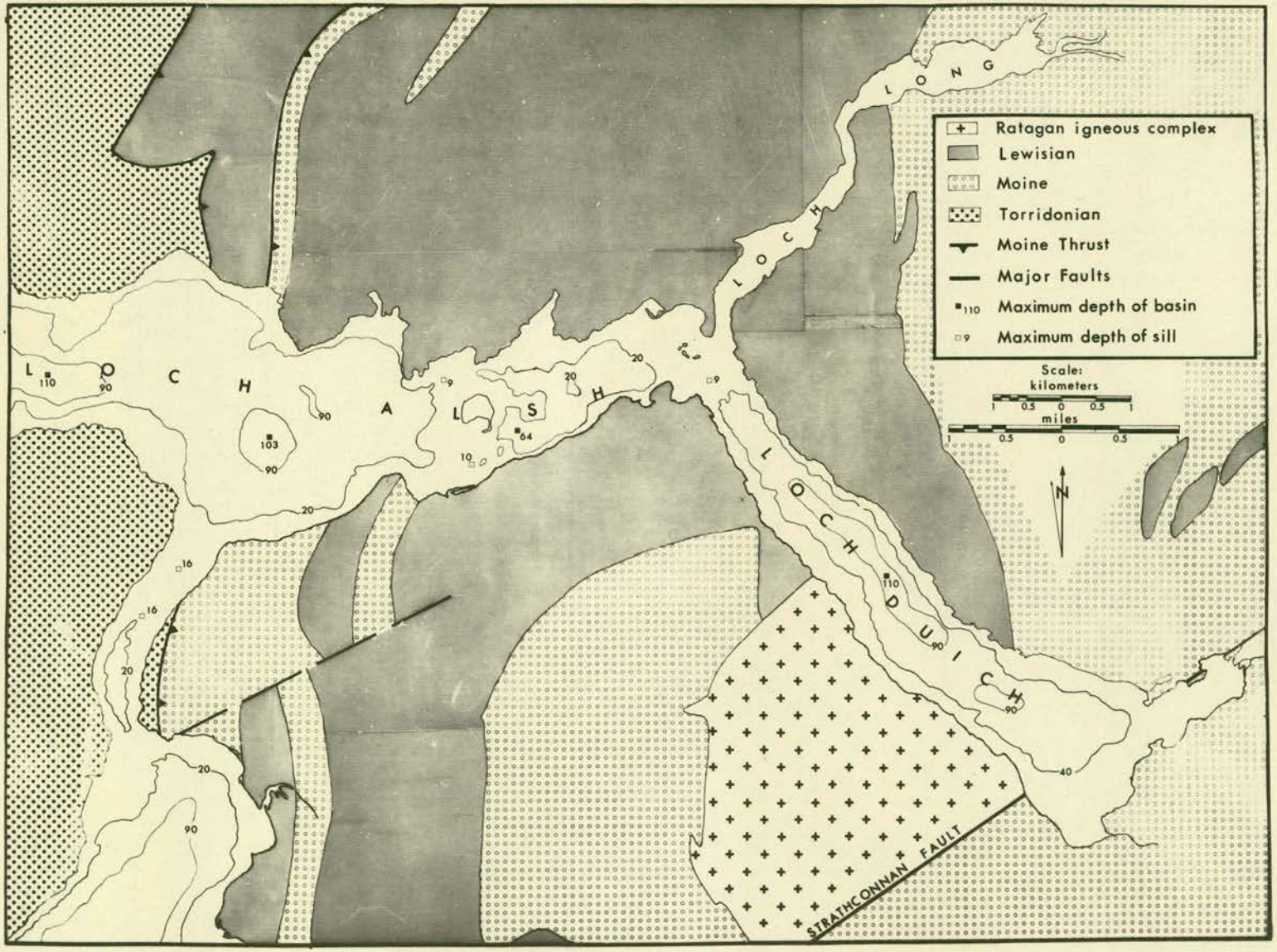
FIG. 2.3; Average Annual Rainfall in Inches 1916–1956 in the Area of Loch Duich



soon after it has fallen on the hills. On the two occasions on which temperature and salinity measurements were made on the waters of the loch, the rainfall had been particularly low in the previous two weeks, and hence the freshwater input from the rivers to the Loch was relatively low (Figs. 4.3 and 4.2).

2.2 Geology of the area (Fig. 2.4)

The area of Loch Duich lies immediately to the east of the Moine thrust. The rocks on the shore of the Loch and to the west consist of mainly Lewisian hornblende and biotite gneiss usually with garnet, biotite amphibolite, eclogites and diopside forsterite marble (Harker, 1941). Intercalated with the Lewisian are bands of Moine psammitic schists; these bands become more abundant to the south and east. In the region of the five sisters of Kintail, the Lewisian is no longer found and the rock is entirely Moine quartz schists and granulites (Johnson, 1965; Harker, 1941). The boundary between the intercalated Lewisian and Moine and the Moine alone is the Strathconnen fault, which runs in a N.E. - S.W. trend from the mouth of Loch Hourn across the head of Loch Duich to Loch Monar. It is the principal tectonic lineation found within the area, though other minor faults are present (Nicholls, 1950), one of which gave rise to a minor series of earthquakes (Magnitude 4) in August 1974; the epicentre being located 8 km below Boc Mor (Figure 2.2). The Strathconnen fault is also the southern boundary of the Glenelg - Ratagan igneous complex. This complex is primarily dioritic in composition, though granodiorite, syenite, adamellite and several ultrabasics are also present (Nicholls, 1950).


Ratagan igneous complex
Lewisian
Moine
Torridonian
Moine Thrust
Major Faults
110 Maximum depth of basin
9 Maximum depth of sill
Scale:
kilometers
1 0.5 0 0.5 1
miles
1 0.5 0 0.5 1
N
LOCH LONG
LOCH ALSH
LOCH DUICH
STRATHCONNAN FAULT
110
90
103
64
20
10
16
40

There is some evidence of minor lead - zinc mineralisation along the Strathconnen fault in the Ratagan forest area, although this is not economically significant (IGS unpublished data). There is no evidence from this study that this mineralisation had any significant influence on the magnitude or the distributions of trace metal in the sediments of Loch Duich.

2.3 Geomorphology of the area

N.W. Scotland was greatly modified by the Pleistocene glaciation (Sissons, 1965). Evidence for glaciation within this area is extensive; fine examples of corries which are found just below the highest peaks of the Saddle and the five sisters of Kintail; Glen Lichd and Glen Shiel are well preserved U-shaped valleys, while the valley of Allt an Leoid is a glacial hanging valley. The confluence of the Glen Lichd and Glen Shiel glaciers caused a considerable overdeepening of the valley, resulting in the fjord system of Loch Duich - Loch Alsh.

It was suggested that the movement of glaciers was controlled by preexisting river valleys and that many of these valleys picked out lines of structural weakness, the axes of folds or faults (Peach and Horne, 1930). In the area of Loch Duich the principal geomorphological features are all perpendicular to the local strike of the rocks, i.e. Loch Duich, Glen Shiel and Glen Lichd, or subparallel to it, i.e. Strath Croe, Loch Long and Loch Alsh (Fig. 2.2). The only glacial feature known to be directly controlled by a tectonic lineament is Strath Croe, which is controlled by the Strathconnen fault.

The two rivers, the Shiel and the Croe, which now flow within the major glens at the head of Loch Duich have had very little effect

on the geomorphology of their valleys, although the River Shiel has eroded into some of the glacial till at the head of its valley. At the mouth of both rivers there are regions of salt flats and small alluvial fans.

CHAPTER 3

SEDIMENT IN LOCH DUICH

3.1 Introduction

It is important in a study of sedimentary diagenesis to know the mineralogy, major element geochemistry, porosity and grain size of the sediment. If the sediment is homogeneous with depth with respect to the mineralogy, grain size and major element geochemistry, then the observed changes in composition of the sediment and pore waters can be interpreted in terms of changes in the non detrital sediment input and diagenetic reactions occurring within the sediment. These parameters were also used to provide information on the direction of derivation of the sediment.

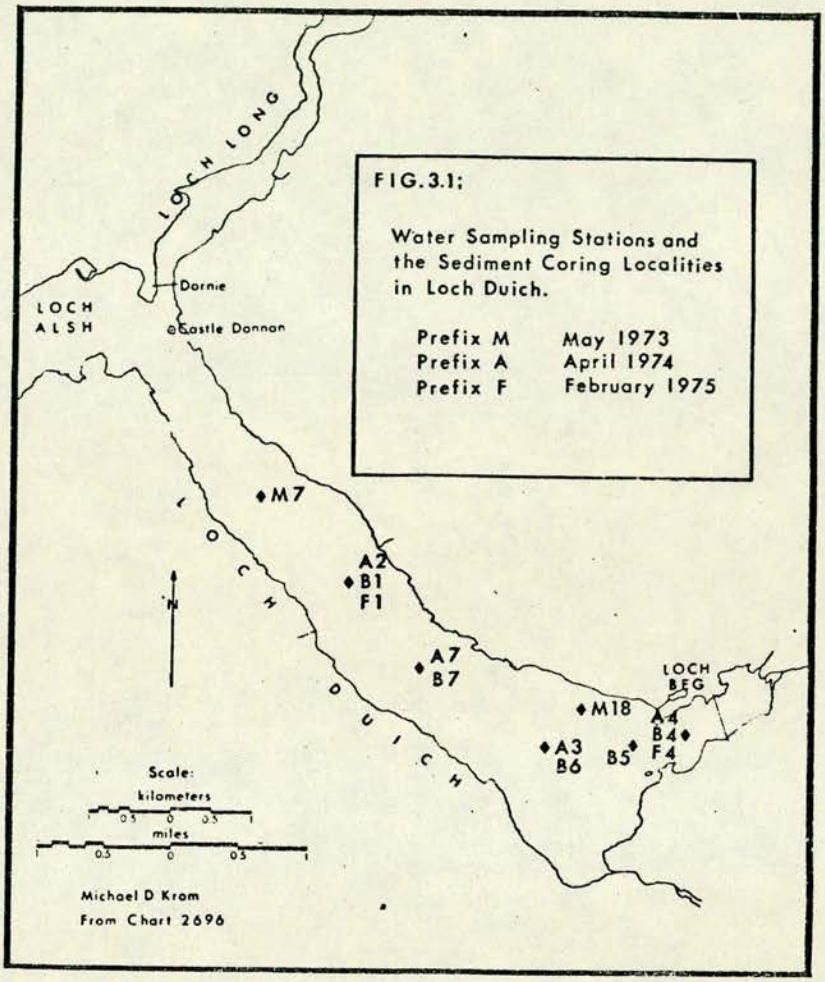
Figure 3.1 shows the sampling stations for the water column and the sediment coring localities.

3.2 General description of the sediment

Two principal types of sediment were sampled in Loch Duich. A grey-black fetid mud was collected from the comparatively flat areas in the central basin and a brown sandy mud with a large number of recognisable mica flakes was sampled in Loch Beg adjacent to the outflow of the River Croe. Within each core there were no colour or lithological changes visible.

3.3 Mineralogy

Core A2D, which was taken from the deepest part of the basin and is considered on geochemical criteria to be a typical basin core



Nomenclature: Stations prefixed by B are the water sampling stations collected in April 1974. Stations prefixed by A are coring localities sampled in April 1974, stations prefixed by F are coring localities sampled in February 1975. In all cases the next number represents the station number followed by a letter A-G which indicates the number of the core collected from a particular coring station. The final number represents the depth in metres from the surface in the water profiles and the depth in centimetres from the top of the core sampled to the top of the subsampled section. Thus A2D20 represents a core section 20-30 centimetres down from the top of the fourth core collected from station 2 in April 1974.

(Chapter 5), was analysed mineralogically by X-ray diffraction, the peaks identified using the tables of Chao (1969). All the samples in the A2D profile show a similar set of peaks which are characteristic of quartz (4.23Å, 3.36Å and 2.45Å), calcite (3.04Å), chlorite (7.07-7.24Å, 3.50Å and 2.56Å), a suite of feldspar minerals (4.00-4.03Å and 3.18-3.21Å) and a micaceous mineral, possibly illite or muscovite, with peaks at 10.04Å, 4.48Å and 2.56Å. All the samples also showed the characteristic halite peak (2.81Å) caused by dry sea salt in the specimen, and some also showed a peak from the aluminium sample container. This suite of minerals (quartz, chlorite, feldspar and poorly degraded mica) is typical of a cool, temperate climate where mechanical weathering is a more important factor than chemical weathering (Biscaye, 1965; Slatt, 1974). Although there is a small quantity of calcite in the form of forsterite marble present in the rock adjacent to Loch Duich (Peach et al., 1910), it is thought likely that the majority of the calcite present in the sediment is biogenic (Davies, 1976). A similar suite of minerals has been found in Bolstadfjord, Norway (Taylor, 1974), Oslofjord, Norway (Doff, 1970), Conception Bay, Newfoundland (Slatt, 1974) and in the North Atlantic adjacent to the temperate and arctic regions (Biscaye, 1965).

In addition, a sample from the surface of core A4 (Loch Beg) was analysed mineralogically and also found to contain quartz (4.23Å, 3.36Å and 2.45Å), feldspar (4.00-4.03Å and 3.18-3.21Å) and chlorite (7.07-7.24Å, 3.50Å and 2.56Å). A series of micaceous peaks were found with similar wavelengths to those found in core A2D (10.04Å, 4.48Å and 2.56Å), however these peaks were relatively much stronger

in core A4, and in addition two other peaks were also found at 13.2Å and 4.92Å, which are consistent with presence of hydrobiotite. No calcite peak was found in the sediment from Loch Beg (A4).

The mineralogy of sediment collected from the rainfall catchment (Fig. 2.2) was analysed and compared to that found in the sediment of Loch Duich and Loch Beg, to see if the provenance of the sediment could be established. A fraction of the sediment was concentrated magnetically using a Franz magnetic separator prior to analysis. The principal components of the sediment were quartz and plagioclase feldspars, while the magnetically separated fraction contained a high proportion of micaceous minerals, biotite and muscovite and their breakdown products hydrobiotite and a chloritoid mineral. These are minerals derived principally from the primary weathering of the Moine series of metamorphics which are found in the catchment area. The major proportion of rocks exposed in the North West Highlands are metamorphic (Lewisian, Moine and Dalradian) or sedimentary rocks derived from them, such as the Torridonian sandstones (Johnson, 1965) and the Jurassic sandstones (Hallam, 1965; Krom, unpublished work), the only major exception being the series of Tertiary igneous complexes (i.e. Mull, Skye, Ardnamurchan). It follows that the sedimentary input into Loch Duich will be mineralogically similar whether it is derived from rocks present in the catchment area or from sediment brought in over the sill by tidal inflow. However, Weaver (1959) noted in a number of localities in the North Atlantic that there tends to be an increase in the relative amount of illite and chlorite and a decrease in kaolinite seawards. The presence of illite and chlorite in core A2D and no hydrobiotite tends to suggest

that the basin sediments are well matured marine sediments derived from outwith the Loch Duich rainfall catchment area, whereas the suite of minerals found in the Loch Beg sediment sample, quartz, feldspar, biotite and/or muscovite, chlorite and hydrobiotite, is very similar to that found in the catchment area.

3.4 Major element geochemistry

Three cores, two from the central basin A2 and F1 and one F4 from Loch Beg, were analysed for the major elements (Al, Si, Ti, Fe and P) by X-ray fluorescence analysis. All the cores that were analysed for trace metals (Pb, Fe, Cu, Zn and Mn) were also analysed for Rb. Previous work has shown that Si, Al and Ti are associated with the detrital fraction of the sediment (Goldschmidt, 1954). Rb is considered to be associated with K (Goldschmidt, 1954), and hence in recent sediments with the detrital phase (Doff, 1970; Taylor, 1974). Doff showed that in sediments collected from Oslofjord, which have a large spread of Al_2O_3 values 8.4 - 15.8%, there was a good correlation between Al and Rb. In Loch Duich the spread of Al values is much less, and hence the graph of Al vs. Rb plots as a spot with the spread of values being within the analytical error.

The results of major element geochemistry analyses for coresF4, A2 and F1 are given in Table 3 I and the analyses of Rb in Table 9 I. The analyses for Si and Ti are also expressed as the element/Al ratios. Table 3 II compares the average values for these ratios from each core to the values quoted for "average" shales in Krauskopf (1965) and Wedepohl (1968). (The errors shown for these averages represent $\pm$ one standard deviation.)

Table 3 I

Major element concentration in the sediments of Loch Duich

Core and depth (cms)		Al %	Si %	Ti %	Si/Al	Ti/Al
F1	0	6.43	19.03	0.43	3.0	0.067
	5	7.01	20.94	0.47	3.0	0.067
	10	6.95	20.75	0.48	3.0	0.069
	15	7.43	21.62	0.51	2.9	0.069
	20	6.60	19.31	0.44	2.9	0.067
	25	7.37	21.68	0.49	2.9	0.066
	30	6.92	20.30	0.46	2.9	0.066
	35	7.23	21.42	0.49	3.0	0.068
	40	7.24	21.34	0.48	2.9	0.066
	45	7.48	22.58	0.52	3.0	0.070
	50	6.91	20.52	0.47	3.0	0.068
	55	7.17	22.07	0.49	3.1	0.068
	60	6.44	19.91	0.43	3.1	0.067
	65	7.03	21.57	0.49	3.1	0.070
	70	6.57	20.09	0.46	3.1	0.070
	75	7.04	21.16	0.52	3.0	0.074
	80	6.52	19.57	0.48	3.0	0.074
A2	0	6.99	21.39	0.46	3.1	0.066
	10	7.20	20.96	0.48	2.9	0.067
	20	7.35	22.08	0.50	3.0	0.068
	30	7.09	21.71	0.50	3.1	0.071
	40	6.60	19.94	0.49	3.0	0.074
	50	6.60	19.89	0.50	3.0	0.076
	60	7.27	21.46	0.49	3.0	0.067
	70	7.10	21.50	0.51	3.0	0.072
	80	6.53	19.51	0.45	3.0	0.069
F4	0	6.87	23.50	0.56	3.4	0.082
	5	7.50	25.50	0.62	3.4	0.083
	10	7.20	24.88	0.65	3.5	0.090
	15	7.64	26.03	0.61	3.4	0.080
	20	7.54	25.36	0.60	3.4	0.080
	25	7.98	26.47	0.65	3.3	0.081
	30	7.78	25.57	0.65	3.3	0.084
	35	7.76	25.14	0.66	3.3	0.085
	40	7.47	23.41	0.63	3.1	0.085

Table 3 II

A comparison of the average value of major element/Al ratios from the basin sediments of Loch Duich and the sediments of Loch Beg to the values quoted for "average" shales and some of the major mineral components identified in the sediment.

Location and No of samples analysed or mineral	Ti/Al	Si/Al	Rb/Al ($\times 10^{-4}$)	Fe/Al	P/Al	Al(%)	Reference
Loch Duich (26)	0.069	3.00	15.7	0.66	0.014	7.3	This study
Loch Beg (9)	0.083	3.34	14.9	0.57	0.017	7.85	This study
Av. shale	0.056	2.98	17.5	0.59	0.0096	8.0	Krauskopf (1965)
Av. shale	0.052	3.11	15.9	0.55	0.0079	8.8	Wedepohl (1968)
Chlorite		0.9					Degens (1965)
Illite		1.5					ditto
Plagioclase	0.01	1.59		0.014			Deer et al. (1962)
Alk. Feldspar	0	3.0		0			ditto
Biotite	0.15	1.64		1.13			ditto
Muscovite	0	1.12		0			ditto
Chlorite	0.01	1.08		0.71			ditto
Illite	0.005	1.13		0.04			ditto

There are relatively small variations with depth in Al content for these three cores; F4 (7.85 $\pm$ 0.22%), A2 (7.14 $\pm$ 0.60%) and F1 (7.26 $\pm$ 0.38%). This shows that the proportion of lithogenous constituents remains fairly constant down the core. Similarly, the values for the analysis of Rb remained relatively constant in each of the cores analysed; F1 (111 $\pm$ 4 ppm), A2 (112 $\pm$ 7 ppm), A7 (112 $\pm$ 7 ppm), A4 (116 $\pm$ 9 ppm) and F4 (117 $\pm$ 7 ppm).

The average Ti/Al and Si/Al ratio likewise shows little variation within each core, demonstrating that the detrital component is constant with depth and can be discounted as an explanation for the observed changes in sediment and pore water geochemistry.

There are, however, significant differences in the geochemical ratios between the core from Loch Beg F4 and the two cores from the central basin of Loch Duich F1 and A2 . The Si/Al ratio for the Loch Beg core is significantly greater (3.34 $\pm$ 0.11) than that for the two basin cores (3.00 $\pm$ 0.07). This latter value compares very closely with the Si/Al ratio for an "average" shale. This is interpreted as being due to a higher proportion of detrital quartz within the sediment from Loch Beg.

The Ti/Al ratio is also greater in the core from Loch Beg (0.083 $\pm$ 0.003) than those for the central basin (0.069 $\pm$ 0.003). Hirst (1962) suggests that a higher Ti/Al ratio is indicative of a larger median grain size, since the sandy fraction tends to contain a larger proportion of Ti bearing minerals; rutile, ilmenite and biotite. The presence of a large proportion of biotite and hydrobiotite in the sediments from the catchment area suggests that this may be a possible source for the excess Ti in the core from Loch Beg.

3.5 Porosity

The porosity of four of the principal cores, on which sediment and pore water geochemistry were investigated, was calculated from the measured water content (Berner, 1971) and the results given in Table 3 III. The porosity of the basin cores is generally higher at the surface (0.84-0.89) than down the core (0.81-0.84), indicating some compaction. The average porosity (0.84 ± 0.02) is significantly greater than the porosity of the cores from Loch Beg (0.79 ± 0.03), which is consistent with the observation that the former is a finer grained sediment than the latter (Pettijohn, 1957). Pettijohn contrasts the available pore space with the total pore space. The total pore space is measured by using the water content data (Berner, 1971), while it is the available pore space which controls the movement of water and diffusion of ions through the sediment. The Loch Beg cores showed no tendency towards compaction with depth and, when squeezed, released the available interstitial water much more quickly and with less pressure than was required to release the same volume from the basin cores. Thus the movement of water and dissolved constituents is thought to be easier in the Loch Beg cores than in the basin cores.

3.6 Grain size

There is no significant variation in the grain size distribution within each core for a series of localities in Loch Duich (Table 3 IV). Davies (1976) examined the general grain size distribution for the surficial sediments within the basin of Loch Duich (Figure 3.2). He showed that the principal basin sediments are a silty mud ($\sim$ 60% clay

Table 3 III

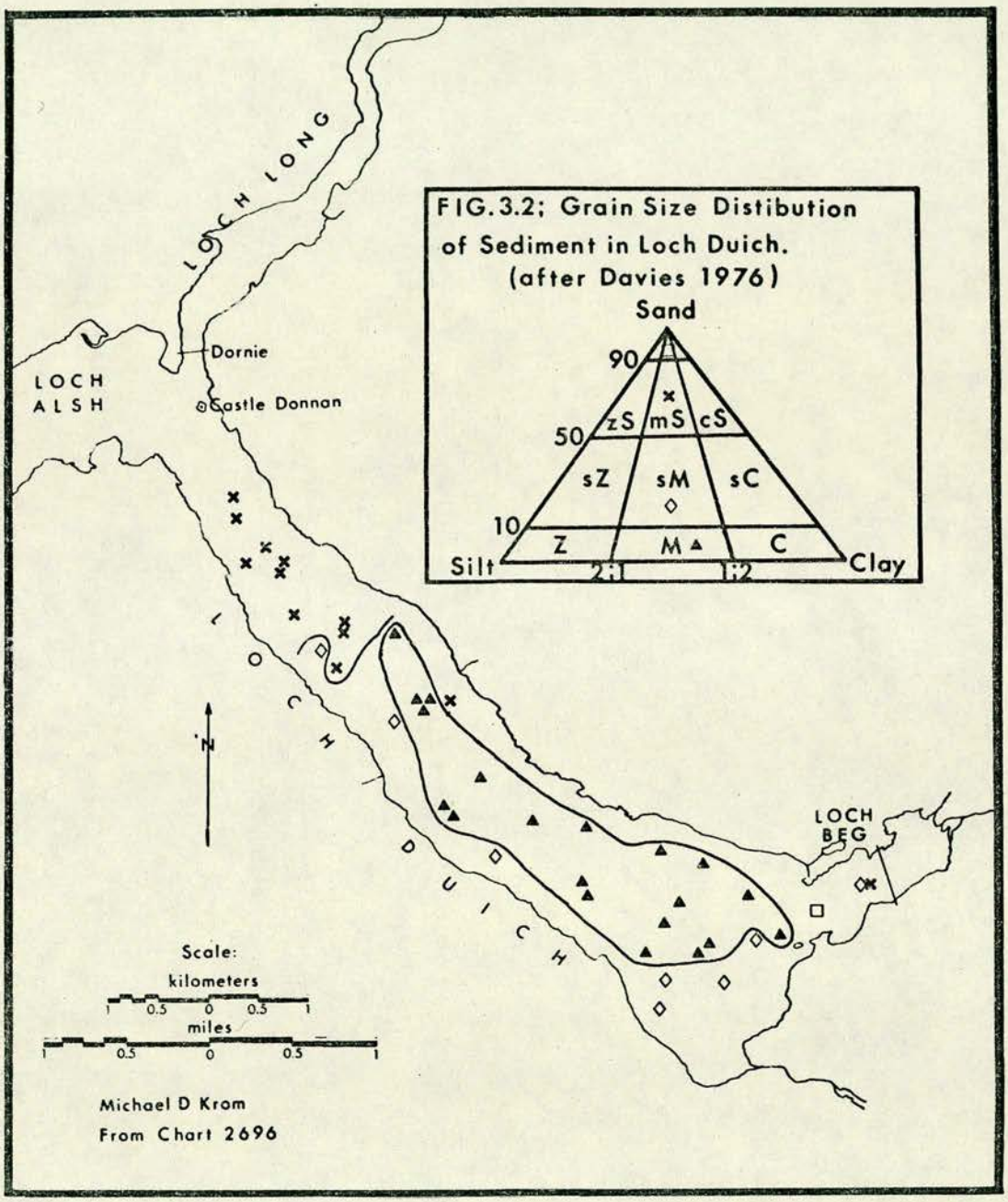
Calculated porosity (Φ) for sediment from 4 cores F1, A4, A2 and F4 from Loch Duich from known water content of the sediment calculated using the method of Berner (1971)

Core and depth		Φ	Core and depth		Φ
F1B	0	0.89	A4A	0	0.78
	10	0.86		10	0.78
	10	0.87		10	0.75
	20	0.86		20	0.73
	20	0.85		20	0.75
	30	0.84		30	0.76
	30	0.85		30	0.78
	40	0.84		40	0.79
	40	0.82		40	0.82
	50	0.83		50	0.84
	50	0.83		50	0.82
	60	0.83		60	0.80
	60	0.82		60	0.81
	70	0.82		70	0.82
	70	0.83		70	0.82
	80	0.87			
Average		0.84			0.79
S.D.		0.02			0.03
A2D	0	0.85	F4B	0	0.87
	10	0.84		10	0.81
	20	0.83		10	0.81
	30	0.81		20	0.76
	40	0.81		20	0.77
	50	0.83		30	0.78
	60	0.81		30	0.79
	70	0.82		40	0.79
				40	0.79

Table 3 IV

Grain size analysis of sediments in Loch Duich (after Davies 1976)

Core	Depth	Pebble	Sand	Silt	Clay
9	0-6		1.1	27.1	71.8
	18-24		2.0	35.7	62.3
	36-42		1.9	39.6	58.5
	72-78		0.8	32.2	67.0
	96-102		0.8	34.0	65.2
6	6-12		3.0	38.7	58.2
	24-30		2.7	35.9	61.4
	54-60		2.3	35.6	62.1
	84-90		9.5	39.8	50.7
7	0-6	1.9	81.1	5.0	12.1
	30-36	1.3	81.9	6.2	10.6
	60-66	2.1	76.3	8.4	13.2
8	0-6		3.6	45.1	51.4
	24-30		3.8	39.6	56.7
	50-54		5.6	40.4	54.1
	66-72		5.5	40.9	53.6
	84-90		9.3	28.8	62.5
1	6-12		4.5	31.5	64.0
	24-30		6.0	30.2	63.8
	50-54		5.8	37.7	56.5
	66-72		2.7	32.2	65.1


LOCH LONG
Dornie
LOCH ALSH
Castle Donnan
LOCH DUICH
LOCH BEG
N
Scale:
kilometers
1 0.5 0 0.5 1
miles
1 0.5 0 0.5 1
Michael D Krom
From Chart 2696
FIG. 3.2; Grain Size Distibution
of Sediment in Loch Duich.
(after Davies 1976)
Sand
90
50
10
zS
mS
cS
sZ
sM
sC
Z
M
C
Silt
2:1
1:2
Clay

size and 40% silt grade), while the sediments from Loch Beg are sandy muds and muddy sands.

Figure 3.2 shows that the sediment in the deepest part of the basin is the finest grained, a mud with less than 2% sand present. To the north-west, in the direction of the mouth of the loch, the sediment shows a coarsening sequence from a mud to a sandy mud to a large area of muddy sand; these changes are not directly related to the bathymetry. The sill of the loch is covered by pebbles (and brittlestars!). To the south-east of the deepest portions of the loch, the bottom remained covered in a mud, even though the depth shallowed from 120 metres to 50 metres. Only immediately adjacent to the mouth of the Rivers Shiel and Croe did the sediment coarsen into a sandy mud and a sand.

This represents an overall pattern in which the grain size becomes finer towards the land with only minor local modifications by river input of sediment. A similar sequence was found in Somes sound (Folger et al., 1972), which was interpreted as being evidence that the major source of supply for the sediment was from the sea by tidal currents.

Samples of sediment from the rainfall catchment area of Loch Duich were collected jointly with Davies from layers immediately below the vegetatively bound soil. The majority of the sediment found was sand or sandy mud, despite searching the region preferentially for flat areas which looked likely to be sources of fine grained (silty) sediment. In addition, the total volume of superficial sediment in these valleys was small; in the valley of Allt an Leoid the geomorphology and the thickness of the sediment above

the bedrock where it was cut into by streams was examined and used to estimate the total thickness of sediment. This was for large areas zero or only a few centimetres, and reached a maximum of approximately seventy centimetres at the bottom of the valley. Below this superficial sediment solid rock was seen to outcrop.

The hills within the catchment area do have some areas of hill peat, although they are not as extensive as in many other regions in the Highlands. This is because the hills are too steep and too quickly drained to favour the growth of peat moss (Peach et al., 1910).

From this survey it was concluded that there was very little fine grained sediment available in the catchment area to provide the extensive silt-clay deposits found in the central basin of Loch Duich, and that the majority of the sediment load in the rivers is sand with some dissolved and particulate peaty material.

3.7 Conclusions

All the cores are homogeneous with depth in those elements which are characteristic of the lithogenous fraction. The total concentrations of Al, Rb, Si and Ti remain constant with depth, showing that the nature of the lithogenous input has not significantly altered in either mineralogy or grain size over the depth of core sampled. As shown in Chapter 7, the total organic matter input has also remained relatively constant through the time of deposition considered. It is thus possible to use comparatively simple models which ignore bulk changes in the geochemistry, mineralogy and grain size of the sediment input to explain the observed changes in pore water and sediment geochemistry.

Table 3 V

Sediment properties of Loch Duich basin cores contrasted with those of Loch Beg

Loch Duich	Loch Beg
Al = 7.14 ± 0.60%	Al = 7.85 ± 0.22%
Si/Al = 3.00 ± 0.07	Si/Al = 3.34 ± 0.11
Ti/Al = 0.069 ± 0.003	Ti/Al = 0.083 ± 0.003
Porosity = 0.84 ± 0.02	Porosity = 0.79 ± 0.03
A black fetid mud.	A brown sandy mud or muddy sand with recognisable micaceous fragments.
The pore waters difficult to remove by squeezing and thus low available porosity.	The pore waters easy to remove by squeezing and thus high available porosity.
Mineralogy: Quartz, feldspar, chlorite, illite/muscovite and calcite.	Quartz, feldspar, chlorite, hydrobiotite and biotite/muscovite.
Organic matter:	
Total organic carbon (TOC) = 5.5%	TOC = 5.8%
C/N = 12.6	C/N = 16.5
I/C surface = 52.8-85.1	I/C surface = 21.7-37.1
% humics = 11-30%	% humics = 42%
anoxic pore waters	oxic pore waters

The significant differences in the sediment properties between the cores from the central basin of Loch Duich and Loch Beg are summarised in Table 3 V. It is suggested that these major differences in the sediment present in Loch Duich compared to that in Loch Beg can be explained by the source of these sediments. Those in the basin of Loch Duich are derived from preexisting marine sediments resuspended and brought in by tidal inflow from beyond the sill, while sediments in Loch Beg represent the submarine expression of the alluvial fan of the River Croe. The differences in pore water geochemistry and trace metals (Chapters 5 and 9) between the cores from Loch Duich and Loch Beg are explained initially in terms of these bulk geochemical and physical properties.

3.8 Sedimentation rate in the central basin of Loch Duich

Three attempts were made to estimate the sedimentation rate within the top metre of the central basin sediments of Loch Duich.

Pollen analysis: Three samples of dried sediment from core A2D, a central basin core, were treated with HF by M. Walker (Geography Department, University of Edinburgh), and the insoluble residue examined microscopically for its pollen content. Remnant pollen was relatively sparse and highly corroded, such that identification was very difficult. It was concluded by Walker that there was not sufficient suitable pollen present to allow any reliable attempt at estimating the sedimentation rate.

Lead-210 analysis: Koide et al. (1973) analysed the lead-210 content of a number of recent sediments from lakes and coastal marine regions. These results were correlated with other methods, such as counting

varves and radiocarbon measurements where appropriate, and found to be comparable. Two sediment samples from core A2D were analysed by Heatherington (DAFS Laboratory, Lowestoft) for Pb-210. However, no Pb-210 was detected within these sediments due to analytical problems.

Geomagnetic analysis: Creer et al. (1972) have developed a method for measuring the remnant magnetisation within lacustrine sediments and relating the values obtained to changes in the earth's magnetic field over the last 13000 years. Bishop (1975) has applied this method to a number of cores collected in the Inner Sound close to the mouth of Loch Alsh. The results Bishop obtained tended to be a single non-specific curve, and hence detailed correlation with the results obtained by Creer et al. (1972) in Lake Windermere is of doubtful significance unless an independent method of dating is used as a check. Two six-metre long cores were obtained from Loch Duich and the remanent magnetism measured in them by R. Thompson (Geophysics Department, University of Edinburgh) using the same analytical technique as that developed by Creer et al.. The resulting curve obtained was non-specific, and thus no estimate of the sedimentation rate could be made.

It is not known whether the failure to obtain any estimate of the sedimentation rate by any of these three methods was due to some inherent property of the sediment or due to individual but different failings in each of the methods tried.

Thus the only possible method for obtaining an estimate of the rate of sedimentation is by using those values obtained for similar near shore coastal marine areas (Table 3 VI). From these results it is suggested that 0.1-0.01 cm/yr is a reasonable estimate for the sedimentation rate in Loch Duich.

Table 3 VI

Sedimentation rates for a series of shallow coastal marine sediments which are comparable to the sediments of Loch Duich

Location	Sed. Rate (cms/yr)	Method of Measurement	References
Inner Sound close to Kyle of Lochalsh	0.02-0.03	Geomagnetism	Bishop (1975)
Northern Inner Sound	0.06	Geomagnatism	Bishop (1975)
Byfjord Sweden	0.5-1	-	Ollaussen (1975)
Baltic Sea	0.14	C^{14}	Erlenkeuser et al (1974)
Saanich Inlet	0.4	C^{14}	Nissenbaum et al (1972)
San Pedro	0.1	Pb^{210}	Bruland et al (1974)
Santa Monica	0.1	Pb^{210}	ditto
Santa Barbara	0.4	Pb^{210} and counting varves	Koide et al (1973)
Baja core	0.27	Pb^{210}	ditto
Loch Duich	0.1	Max. dissolved sulphide	Goldhaber and Kaplan (1975)

CHAPTER 4

HYDROGRAPHY OF LOCH DUICH

4.1 The bathymetry of Loch Duich

Loch Duich is part of a complex set of restricted basins which interconnect with the Atlantic Ocean. Loch Duich is the innermost of these basins (Fig. 2.4). At the north end of Loch Duich it is joined by Loch Long. To the west is Loch Alsh, which has itself two basins, the inner basin, east of Glas Eilean, which has a maximum depth of 60 metres and a sill of 10 metres, and the outer basin with a maximum depth of 120 metres. The outer basin has two outlets to the unrestricted sea, Kyle Rhea (16 metres deep) to the south and Kyle Akin (16 metres) to the west.

Loch Duich is a typical fjord as defined by Holmes (1965). It has a maximum depth of 120 metres and a sill with a maximum depth of 10 metres. The bottom of the loch is relatively flat with steep sides. At the head of the loch there are three embayments, the Bay of Inversheil and Ratagan Bay, which are caused by the alluvial fan of the River Shiel, and Loch Beg, which is immediately adjacent to the alluvial fan of the River Croe and has a maximum depth of 24 metres.

The sill was found to be overlain by pebbles. It was known that Eilean Tioran was formed from glacial till and that, though the rocks outcropping at Eilean Donnan and Totaig are both Lewisian, they are not of the same type (May, pers. comm.). It is suggested that the sill of Loch Duich is a terminal moraine in which the fine grained

sediment has been winnowed out by tidal scour. It is not known whether the position of this moraine is controlled by an underlying band of resistant rock.

4.2 Hydrography of Loch Duich

Temperature and salinity were measured using an N.I.O. portable salinity-temperature bridge. Readings were taken in May 1973 and April 1974. Oxygen in the water column was measured by a Winkler titration on samples collected in April 1974. For a complete discussion on the results of the hydrography collected jointly by Ian Davies and myself in May 1973 see Davies (1976). The following is a brief resume of those results and the additional data collected in April 1974.

Figure 4.1 represents a longitudinal profile of Loch Duich, showing the temperature and salinity contours constructed from the data collected jointly by Ian Davies and myself in May 1973. The water was not sampled at any particular state of the tide, and hence the results are a mean value. The water column is a three layer system; an upper layer, which is confined within the top 5-10 metres of the loch, had a higher temperature (9-11^{o}C) than the water below ($\sim 8^{o}$C) and a somewhat lower salinity ranging from 25^{o}/oo at the head of the loch to 32.5^{o}/oo at its mouth, compared to $> 33^{o}$/oo for the body of water below. The middle layer extended from 10-60 metres and had a characteristically higher salinity than the water both above and below it. The bottom layer had a somewhat lower salinity than the middle layer, but remained stable because it was colder, the temperature difference being 0.5^{o}C.

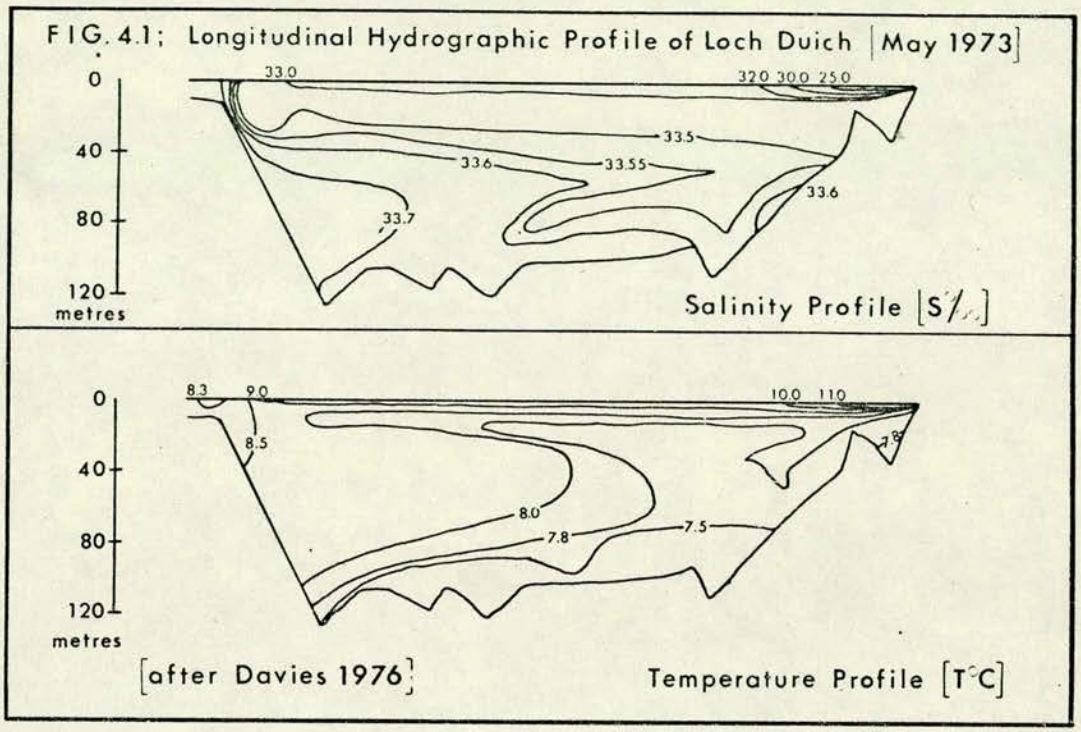


FIG. 4.1; Longitudinal Hydrographic Profile of Loch Duich [May 1973]

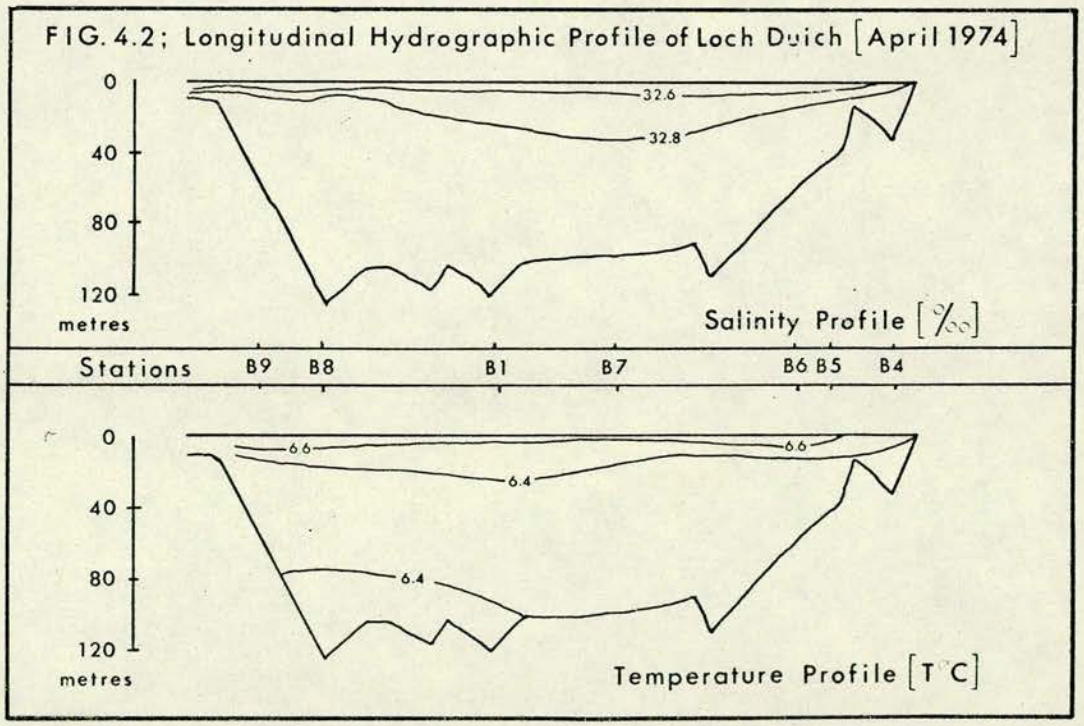


FIG. 4.2; Longitudinal Hydrographic Profile of Loch Duich [April 1974]

Table 4 I

Oxygen saturation (%) in the water column of Loch Duich (April 1974)

Depth (metres)	Station B4	Station B3	Station B7
0	100		115.6
5	99.9	102.4	110.4
10	94.6	100.9	102.0
15	94.0	99.2	
20		97.6	97.3
30		94.7	96.0
40		95.0	95.0
50			94.3
60			96.8
75			93.6
85			98.0

The boundary between the top and middle layers represents a pycnocline which is relatively weak because there was considerable mixing of waters across this boundary, the salinity of this upper layer increasing from the head to the mouth of the loch. This is a typical summer circulation pattern of a fjord with a low freshwater input and a high tidal range (Pickard, 1963; Bowden, 1967). The tidal range in Loch Alsh is 5 metres (Admiralty chart No 2676), which compares to an average of approximately 1 metre for the fjords in the west of Norway (Strøm, 1936).

The profile of temperature and salinity constructed from data collected in April 1974 (Fig. 4.2) showed the loch was much less stratified than it was in May 1973, the temperature difference between surface and bottom waters being 0.6°C as compared to ~3.5°C, and the salinity difference being 0.4°/oo compared to approximately 8.6°/oo. The water column was thus less stable than in May 1973 because of the smaller density difference between the surface and bottom waters, and hence was well mixed.

The concentration of oxygen in the water column depends on the vertical and horizontal mixing, and on plankton photosynthesis and respiratory processes. Fjord environments are primary regions where anoxic conditions can develop in the water column due to topographic restriction of water circulation (Strøm, 1936; Pickard, 1961 and 1963). The oxygen results collected in April 1974 are given in Table 4 I. The water column in Loch Duich and Loch Beg was virtually 100% saturated with oxygen. The values in excess of 100% show that oxygen produced by planktonic photosynthesis is being lost to the atmosphere. The homogeneity of oxygen values confirms the temperature-salinity

results, that Loch Duich was well-mixed at the time of sampling. No oxygen results were available from Loch Duich at a time when stratification in the water column was observed. However, Price and Calvert (1973) show that the oxygen level in the deepest part of the inner basin of Loch Etive, a more restricted basin than Loch Duich, was 40% oxygen saturated when sampled in July 1970. At that time, the loch was highly stratified, and since organic production in the photic zone is at a maximum at that time of year, it is expected that there would be the maximum oxygen depletion in the lower layers. Thus it is suggested that, although some stratification occurs in Loch Duich, there is sufficient tidal mixing to ensure that the entire water column remains oxic at all times.

4.3 Geochemistry of suspended particulate matter

Dissolved and particulate matter is introduced into the water column via rivers and in the inflow of sea water over the sill. The material coming down the river is primarily affected by the change in energy and ionic environment on reaching the sea; a large proportion of the suspended and bed load is deposited immediately on the alluvial fan. The fraction which is dissolved or fine enough to be carried out into the loch may be altered by processes of cation exchange and flocculation (Müller, 1967). Information on the nature of the flocculant can be obtained from analysis of the particulate matter in the surface brackish waters of the sea loch.

Biological processes which occur in the photic zone result in the fixing of inorganic anions (e.g. CO_2, NO_3^-, PO_4^{3-}, SiO_2) and cations (Ca^{2+}, Mg^{2+}, trace metals) into the planktonic material.

These form a high proportion of the particulate matter found within the upper layers. After death, these organisms fall through the water column and onto the sediment. A fraction of the organic matter is decomposed in the water column with a resulting release of nutrients, while the remainder falls to the bottom and is incorporated into the sediment.

All detritus, before it becomes incorporated into the sediment, was at one time particulate matter in the water column. The relation between the bulk analysis of particulate matter in the water column and the underlying sediment is a complex one, principally because of the different settling rates of the components which make up the sediment. Geochemical analysis enables these differences to be examined and also gives information on some of the surface processes at the sediment-water interface.

This data adds to the results collected from other fjord environments in Norway and Scotland (Taylor, 1974; Price and Calvert, 1973 and Skei, 1975).

Five profiles of particulate matter were taken during the trip in May 1973, the stations sampled are shown in Figure 3.1. The chemical composition of the particulate matter was measured by an X-ray emission analysis following the method of Price and Calvert (1973). The concentrations of Si, Al, Ti, Fe and P were measured and the results given in Table 4 II. Scans were run for Zn, Pb and Cu, but these elements were found to be below the detection limits of the method, 0.1 μg (Price and Skei, 1975).

Results: Detrital elements

Following Spencer and Sachs (1970) and Price and Calvert (1973),

Table 4 II

Geochemistry of suspended particulate matter (µg/kgSW)

Station and depth (metres)		Fe	Si	Al	P	Ti
B1	5	43.1	657	66.3	26.8	3.60
	10	7.7	122	11.8	1.3	0.54
	15	24.5	461	40.2	15.1	2.39
	20	38.8	554	59.2	14.7	3.47
	30	31.9	319	57.3	2.5	3.07
	50	26.7	258	41.2	3.1	1.98
	80	30.1	341	53.9	5.6	2.78
	100	4.8	83	9.1	0.4	0.55
B3	5	56.5	1036	81.2	41.3	4.55
	10	38.1	798	54.5	32.3	2.98
	15	55.5	804	90.6	21.3	4.93
	20	40.2	360	71.4	4.8	4.35
	30	16.7	165	29.1	2.1	1.73
	50	69.9	452	110.5	4.1	6.11
B6	0	31.7	640	44.2	27.9	2.42
	5	34.4	722	51.9	32.4	2.84
	10	18.8	420	28.7	11.5	1.85
	20	36.7	358	61.1	4.7	3.19
	30	154.1	961	225.4	6.0	13.50
	40	112.8	702	162.8	8.4	10.06
B7	0	38.0	599	35.8	24.1	3.80
	5	27.5	694	44.6	33.5	2.61
	10	32.9	648	53.7	19.4	2.67
	20	30.6	284	44.1	4.7	2.94
	30	55.4	427	85.1	5.3	5.08
	40	27.9	275	47.4	3.1	2.43
	50	92.3	675	145.7	6.3	8.40
	60	92.3	653	146.5	5.5	8.05
	75	128.7	832	185.4	6.8	10.21
	85	121.6	835	177.3	9.6	9.68
B4	0	58.7	619	77.3	17.2	4.69
	5	38.5	621	65.3	20.8	3.53
	10	58.0	540	88.0	13.3	5.17
	20	87.7	577	126.4	6.3	8.21
Analytical precision (Skei 1975)		1%	6%	2%	4%	5%

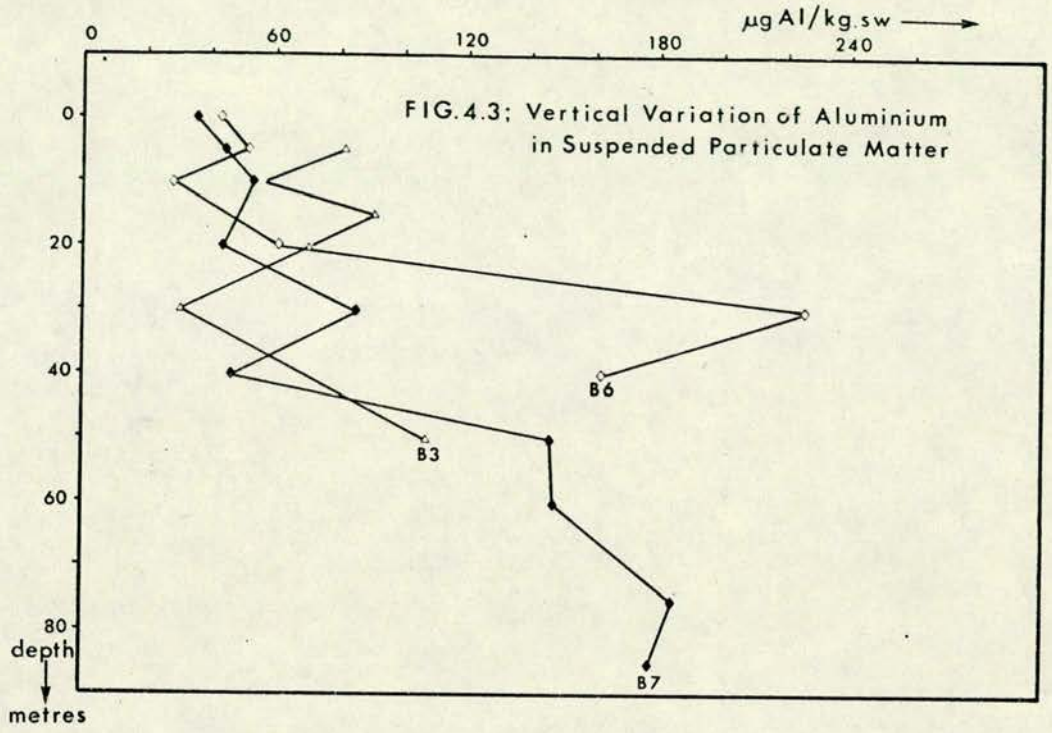


FIG. 4.3; Vertical Variation of Aluminium in Suspended Particulate Matter

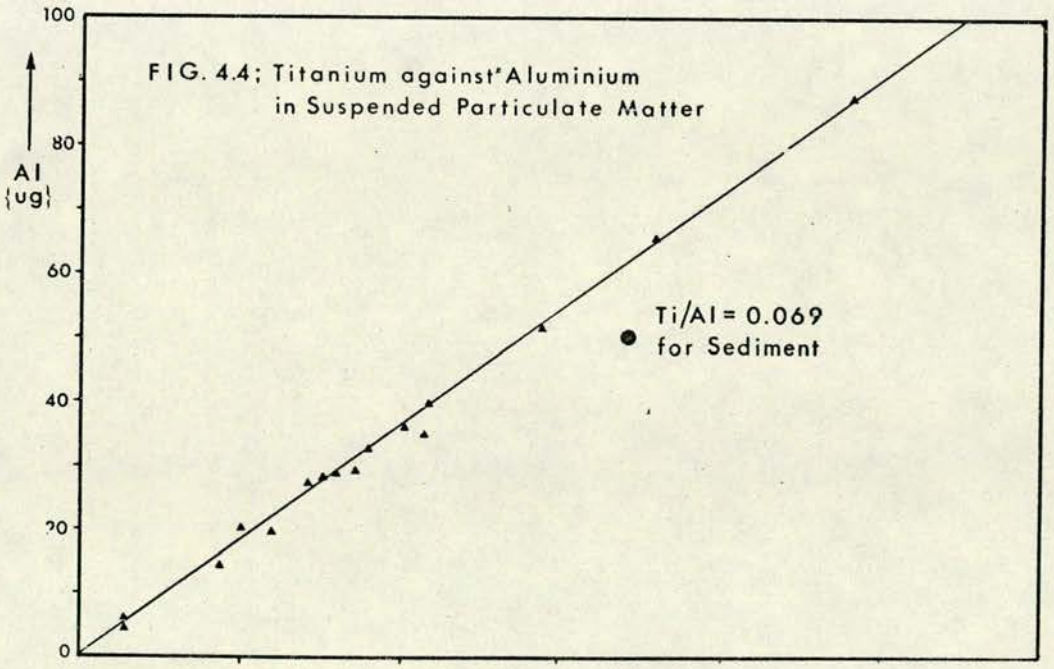


FIG. 4.4; Titanium against Aluminium in Suspended Particulate Matter

the quantity of terrigenous detritus at any level in the water profile can be inferred from the level of aluminium. Figure 4.3 shows the profiles of aluminium in the water column. The absolute values for aluminium and titanium concentrations and therefore of total inorganic detritus compare closely with those obtained for the particulate matter in Loch Etive by Price and Calvert (1973); aluminium in Loch Etive was 7.6-76.0 μg/litre compared to 4.5-103 μg/litre in Loch Duich, while titanium in Loch Etive was 0.39-4.70 μg/litre compared to 0.27-6.16 μg/litre for Loch Duich. There was an irregular increase in aluminium from the surface to the bottom. In the absence of a marked thermocline, detritus can be resuspended from the sediment by the benthos (Spencer and Sachs, 1970) and then, under the action of mixing due to tidal currents, is able to reach the surface (Folger et al., 1972). In a water column where turbulent mixing is not great, such as the inner basin of Loch Etive, this detritus will gradually fall back to the sediment and there will be a regularly increasing aluminium profile (Price and Calvert, 1973). The somewhat irregular profile observed in Loch Duich was due to turbulent mixing processes which occur in the water column and to the possible introduction of detritus by tidal inflow. At the time of sampling, the contribution of detritus from the river was considered to be negligible, as shown by the low concentration of aluminium and titanium in the suspended material above the pycnocline.

Titanium correlates very closely with aluminium (Linear regression coefficient = 0.99, Figure 4.4), showing that it was associated with detrital material (Price and Skei, 1973; Taylor, 1974). The Ti/Al ratio was very constant (0.058) within the whole

water column and less than the ratio in the underlying sediment (0.068). The Ti/Al ratio is dependent on the grain size of the detritus (Price and Calvert, 1973), the finer fraction having a smaller ratio (Hirst, 1962), hence the observed difference is interpreted as being due to a smaller grain size in the water than in the sediment.

Biogenic elements: Silicon

The silicon found in particulate matter is present in aluminosilicates, quartz and in the skeletal material of plankton principally diatoms (Price and Calvert, 1973). The depth profile of Si/Al (Figure 4.5) shows that there was a large excess of silicon in the upper layers where biological productivity was at its greatest (Loder and Hood, 1972).

The Si/Al ratio from 30 metres to the bottom was relatively constant (Fig. 4.6). This ratio 4.0 - 6.0 was considerably in excess of the Si/Al ratio (approximately 3.0) which was measured in the underlying sediment. In order to explain this observation, each of the principal components of the detritus was considered as a possible source for this excess. The principal clays found within the sediment are illite and chlorite, which have Si/Al ratios of 1.5 and 0.9 (Kauskopf, 1965) respectively, and thus cannot have contributed to this excess. Quartz is an unlikely source, since if both clays and quartz are introduced into the water column simultaneously, the quartz will tend to fall to the bottom more rapidly than clays or mica because of its greater weight to surface area ratio. The most likely source of silica is siliceous plankton debris, either dropping down from the productive zone or resuspended from the bottom. This

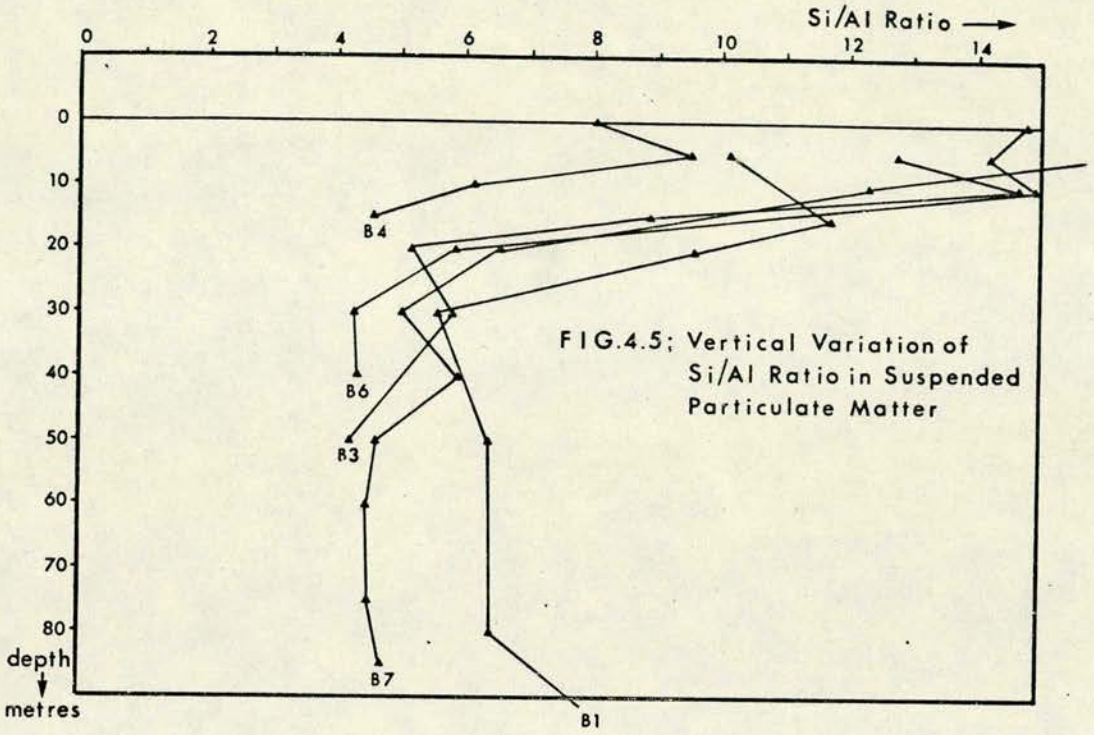


FIG.4.5; Vertical Variation of Si/Al Ratio in Suspended Particulate Matter

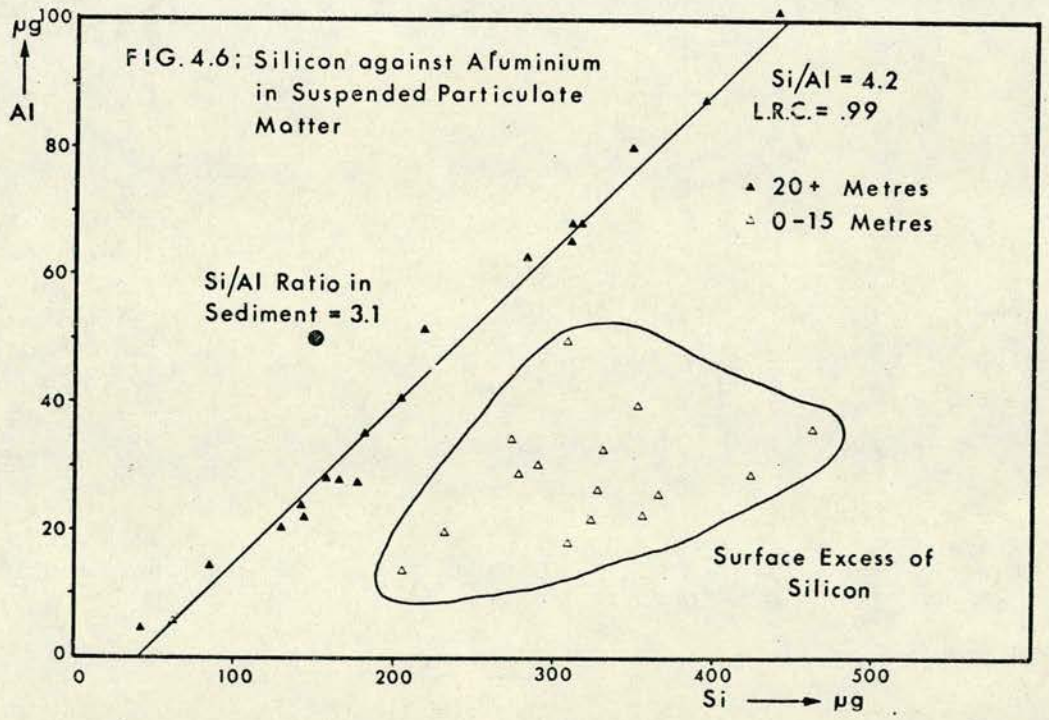


FIG. 4.6; Silicon against Aluminium in Suspended Particulate Matter

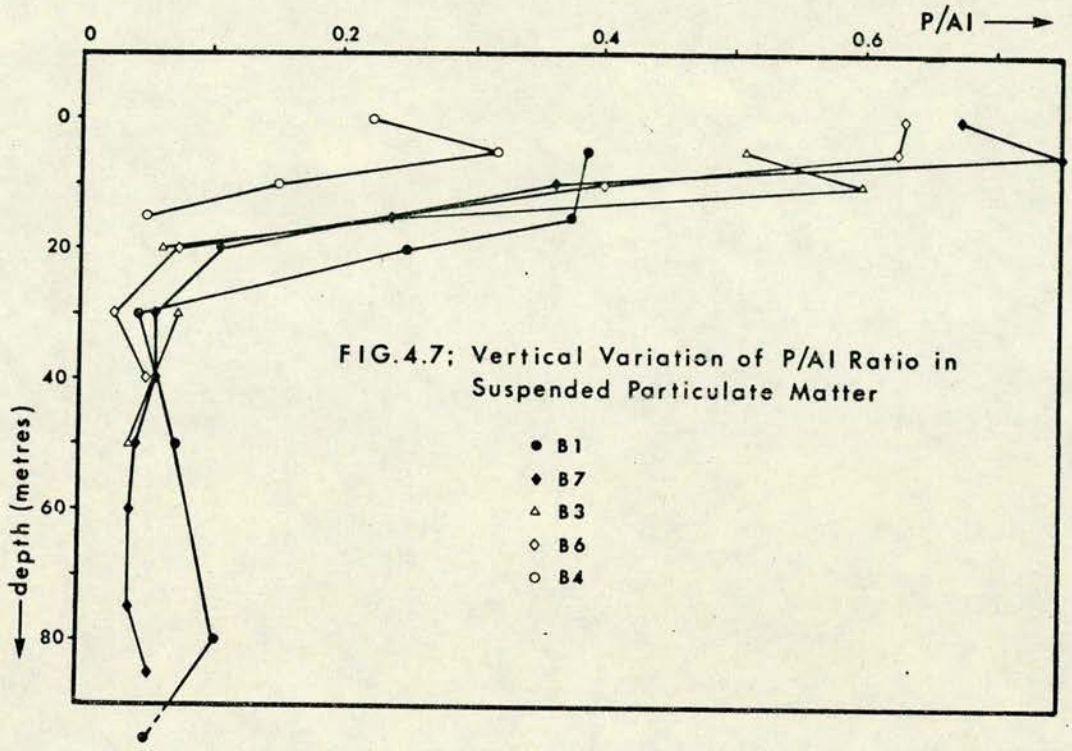


FIG.4.7; Vertical Variation of P/Al Ratio in Suspended Particulate Matter

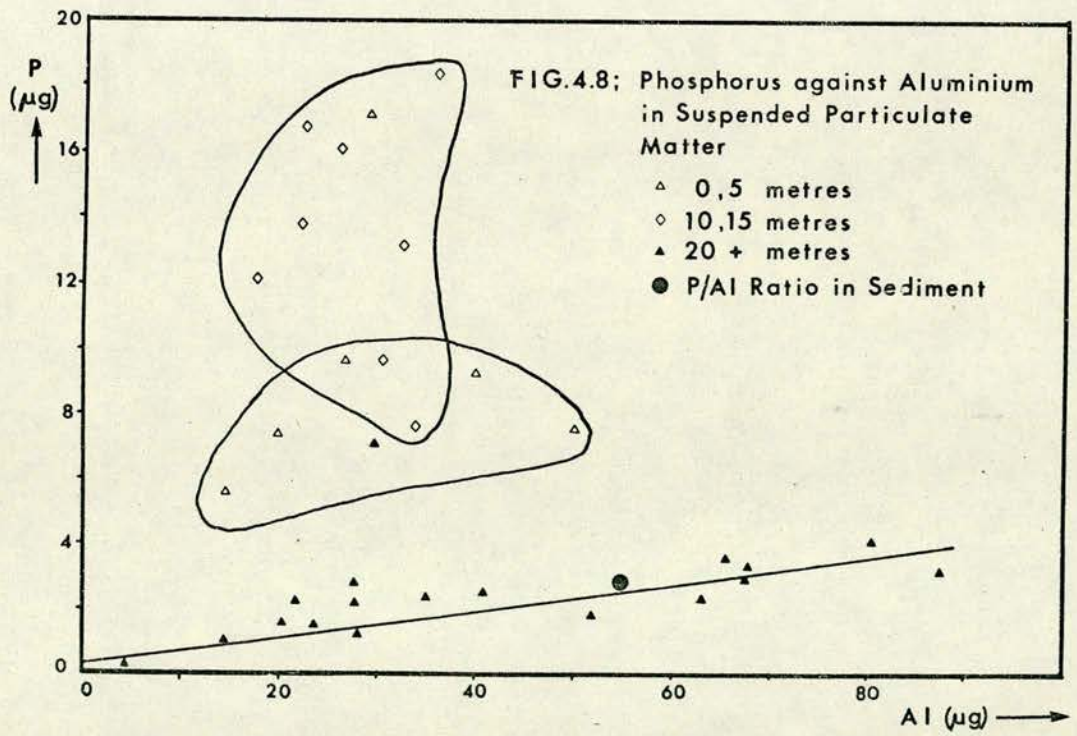


FIG.4.8; Phosphorus against Aluminium in Suspended Particulate Matter

material is very light and tends to deposit slowly. The high values of Si/Al ratio in the top 30 metres of the water column are due to the presence of a large number of live siliceous plankton; below this depth, conditions are no longer suitable for photosynthesis, and although siliceous frustules are seen, they are mainly in the form of fragments. The constant value of Si/Al ratio below the productive zone (0 - 30 metres) suggests that there is very little dissolution of silica in the water column despite the fact that sea water is considerably undersaturated with respect to silica (Armstrong, 1965). This is due to the kinetics of dissolution, which are slow relative to the deposition rate in 100 metres (Martin, 1970). Once incorporated into the sediment, these diatoms dissolve and cause an accumulation of silica within the pore waters (Davies, 1976).

The depth profile of P/Al (Figure 4.7) was similar to that of Si/Al, and showed a considerable excess of non detrital phosphorus in the top 30 metres. The greatest concentration of particulate phosphorus, and by inference particulate organic carbon, was found in the top 5 metres with a lower concentration between 10 and 20 metres.

Figure 4.8 shows a plot of particulate phosphorus vs aluminium with the points grouped according to their depths. Below twenty metres there is a very constant value for the P/Al ratio (0.054), which is very similar to that of the average for the underlying sediment (0.052). The excess of phosphorus over aluminium is depth dependent, the top 10 metres having the greatest excess (P/Al = 0.0525 (av)) with the next 10 metres having a somewhat smaller excess (P/Al = 0.207 (av)). The significant grouping of samples with high particulate phosphorus above 20 metres suggests that the organisms

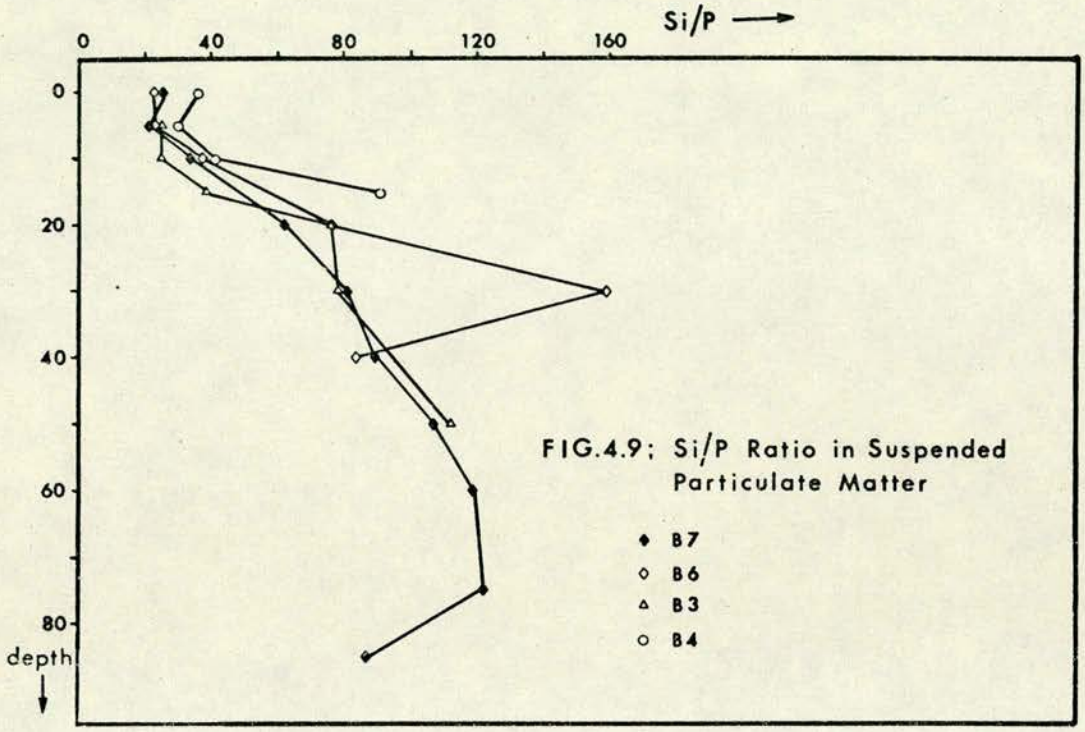


FIG.4.9; Si/P Ratio in Suspended Particulate Matter

on sinking below 20 metres rapidly lose a proportion of their phosphorus, which is then recycled back into the photic zone. The depth profile of Si/P (Figure 4.9) compares the relative loss of silicon and phosphorus from biogenic material with depth. There is an increase of this ratio with depth from ~25.0 at the surface to values in excess of 100 at depth. This shows that phosphorus is recycled more rapidly than is silicon, which reflects the different forms in which these two elements are present in plankton, the former principally in the protoplasm, while the latter is mainly skeletal. The loss and recycling of phosphorus in the upper layers of Hardanger fjord, Norway was also observed by Price and Skei (1975).

Price and Calvert (1973) found a correlation between free iron and total phosphorus in the particulate matter in Loch Etive, which they interpreted as being due to the presence of a ferriphosphate phase. Iron and phosphorus do not correlate in Loch Duich, showing that ferriphosphates, if present, represent an insignificant fraction of the iron.

Iron

Figure 4.10 shows the relationship between iron and aluminium. The linear relationship (LRC = 0.98) suggests that the occurrence of iron in the particulate matter of Loch Duich is dominated by aluminosilicates. The Fe/Al ratio (average = 0.635) is very close to that of the underlying sediment (0.65). However, the samples taken from the surface and those taken from closest to the sediment interface both show a small but significant excess of iron.

The excess iron found at the surface was in the relatively less saline water above the pycnocline (Figure 4.11). This excess was

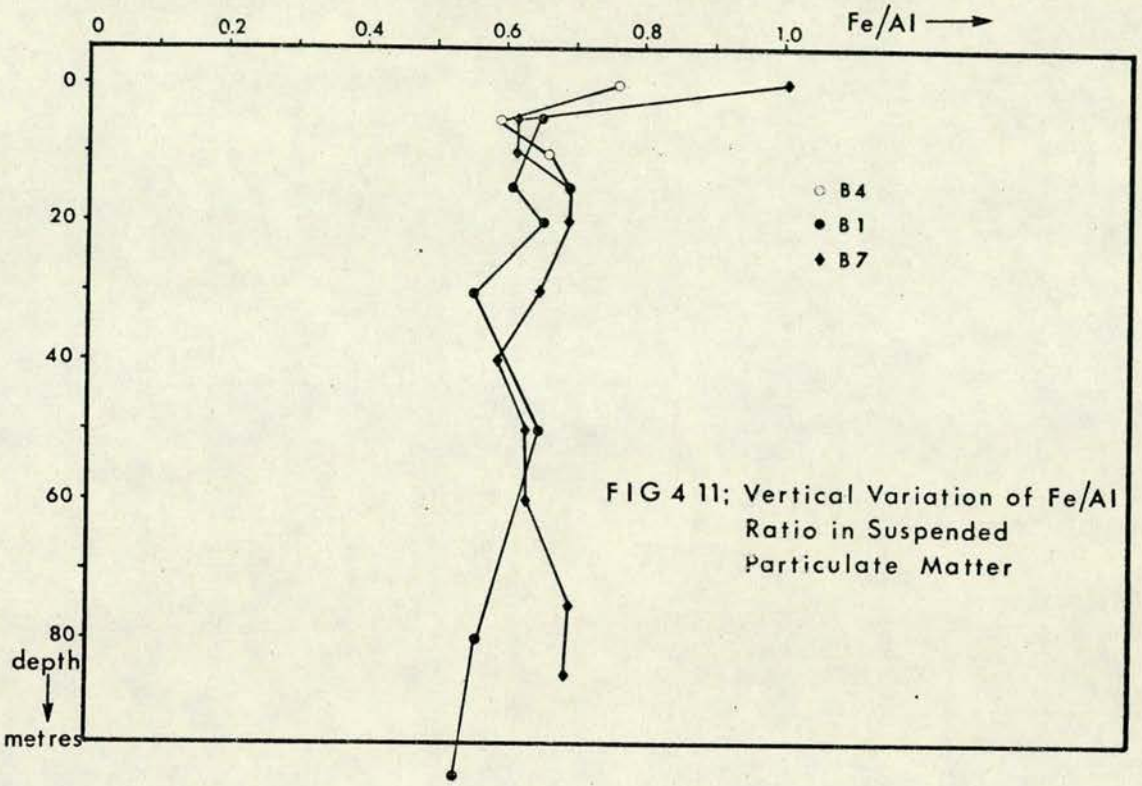


FIG 4 11; Vertical Variation of Fe/Al Ratio in Suspended Particulate Matter

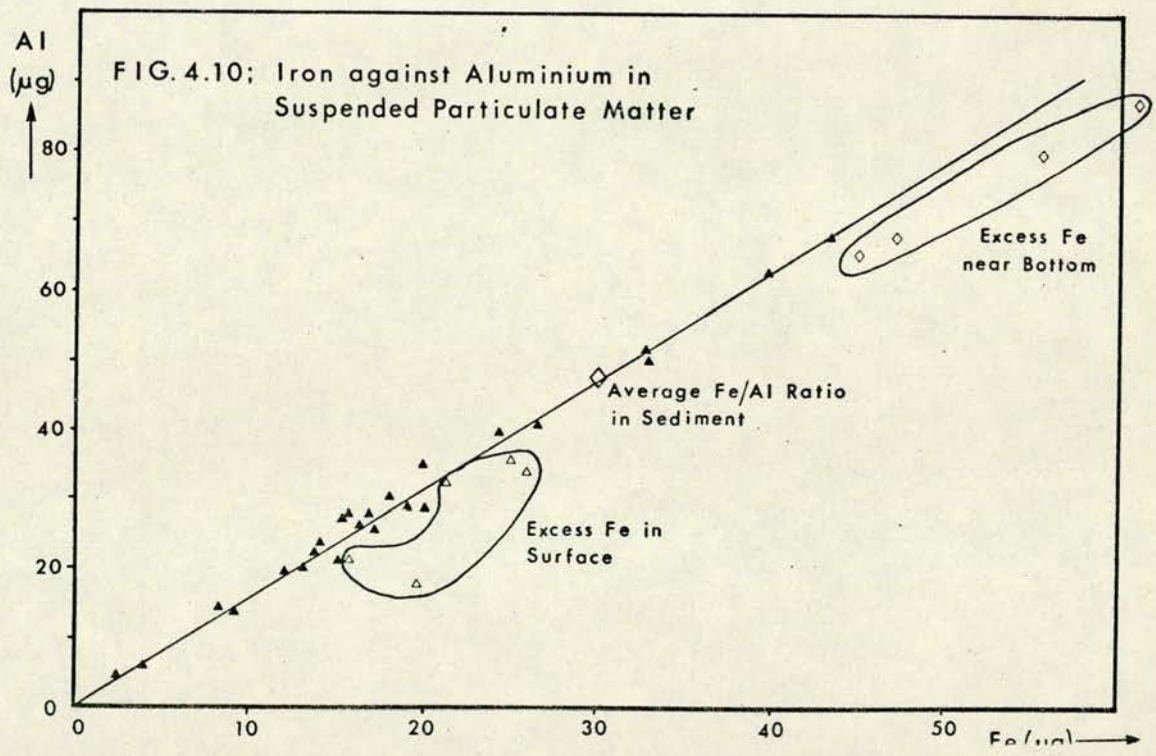


FIG. 4.10; Iron against Aluminium in Suspended Particulate Matter

not associated with the layers of maximum organic productivity (0 - 30 metres), and thus cannot be due to uptake of iron by plankton. There is no evidence of an increase of aluminium or titanium above the pycnocline, and thus the excess iron is not associated with an aluminosilicate phase, as was found in the surface layers of the Gulf of Maine (Spencer and Sachs, 1970). The correlation of iron with the less saline surface water suggests that the excess particulate iron was derived from the river. It has been noted that fine grained material which is derived from the river can be carried as particulate matter above the pycnocline (Sundby, 1974). This phenomen has been observed directly by divers in the Scottish sea lochs. After a period of heavy rain, when the dissolved and particulate sediment load is at a maximum, a surface layer of brown water (a few feet in thickness) containing a high particulate load is often observed (H. Anderson, pers. comm.). The water column in Loch Duich was sampled after a long dry spell when the run off was low, and the sediment input from the rivers was therefore correspondingly low. It is for this reason that there was only a small excess of iron. The rivers that drain into Loch Duich flow through an area containing small areas of peatlands. Water flowing over such terrain tends to accumulate humic and fulvic acids (Shapiro, 1957). These humic and fulvic acids are very strong chelators of metals, particularly iron (Shapiro, 1964; Ghassemi and Christman, 1966; Khan, 1969; Schnitzer, 1969; Schindler et al., 1972). The humic material from fresh water sources is known to flocculate on contact with saline water (Sieburth and Jensen, 1968a). This flocculant has been analysed in a series of laboratory experiments by Sholkovitz (1976). He found an Fe/Al

ratio = 7-21 compared to 0.64 for the detrital particulate matter in the water column in Loch Duich. Sholkovitz (1976) has explained the surface excess of iron and phosphorus found by Price and Calvert (1973) in Loch Etive by the formation of an iron-humate-phosphate complex. Calculations show that if one assumes an Fe/Al ratio = 0.6 for detritus and Fe/P ratio = 20 for the humate complex, then although there is an excess of 18-45% iron above the background level, the phosphorus present as a humate represents only 1-3% of the background and hence would not be detectable. It is suggested that the excess iron observed in the surface waters of Loch Duich was derived from the flocculation of humic acids at the fresh water - sea water interface; the humic acids originating from peat soils in the catchment area. A proportion of this flocculant settled immediately with the majority of the detritus and results in a high proportion of the organic matter (42%) in the sediments of Loch Beg being humic acids; the remainder was carried out in the fresher water above the pycnocline.

The excess Fe (approximately 10%) found in the water column samples closest to the sediment may be evidence for the presence of an oxide-hydroxide phase caused by Fe (and Mn) diffusing out of the reducing sediment into the overlying sea water. Note that an excess of Fe (and Mn) related to the redox boundary has been found in the waters of the Black Sea (Spencer et al., 1972) and Bolstadfjord (Taylor, 1974).

The layer formed on the sediment surface from the precipitation of this phase, which is characteristically brown in colour, was observed directly only once because there was a splash effect with the

gravity corer used, which meant that the top 2-3 centimetres, which contains this phase, was not sampled.

4.4 Summary

Loch Duich is a typical Scottish fjord, the water circulation can be classified as a two layer flow with considerable vertical mixing across the boundary. The freshwater input is variable, but was low on the two occasions when the temperature and salinity were measured due to unusually low rainfall. The water column was well mixed when sampled in April 1974. There was evidence of some vertical stratification in May 1973, when the particulate matter profiles were collected, however the basin waters remain well oxygenated throughout the year due to the large tidal range which effectively mixes the water.

The low freshwater input carried very little detrital material into the loch, although there was evidence of a small quantity of iron-humate flocculant present above the pycnocline.

In the upper layers, 5-30 metres, there was a layer of intense biological productivity with a large excess of phosphorus and silicon. Within the water column it was not possible to differentiate between resuspended sediment and detritus brought in during the tidal cycle. It is suggested that bulk sediment movements occur at times of storms (Beer and Gorsline, 1971), and thus the majority of the detritus in the water column at the time of sampling was due to resuspension. The somewhat higher Ti/Al and Si/Al ratios are interpreted as being due to a smaller grain size predominating in the resuspended matter. A similar resuspension of sediment has been demonstrated in the Gulf

of Maine (Spencer and Sachs, 1970), in Hardangerfjord (Price and Skei, 1975) and in the Gulf of St. Lawrence (Sundby, 1974).

CHAPTER 5

THE GEOCHEMISTRY OF PORE WATER ANIONS

5.1 Changes in pore water anions during diagenesis

The principal changes in the chemistry of the interstitial waters of recent sediments result from microbial respiration. A sequence of distinct biogeochemical zones can be defined by the principal oxidant used in respiration. Figure 5.1 is a diagrammatic representation of the characteristic succession of these zones in a coastal marine sediment.

The recognition of the biogeochemical zones is used as a framework within which to discuss diagenetic changes of dissolved trace metals, organic matter and other non detrital sedimentary material. The results obtained are thus generalised to other coastal marine areas which show a similar sequence of biogeochemical zones.

Organisms obtain their metabolic energy by converting thermodynamically unstable organic matter to more stable byproducts. The organisms act as catalysts to incipient reactions and utilize the free energy released. Those which derive the highest energy yield from the organic detritus are favoured; they will dominate the population until their specific oxidant is exhausted, the next most efficient species will then dominate. The principal reactions which occur in respiration are represented in Table 5 I. Claypool and Kaplan (1974) present a value for the energy released assuming that the organic matter used was glucose under standard conditions. Although the numbers are not strictly applicable, they show clearly the

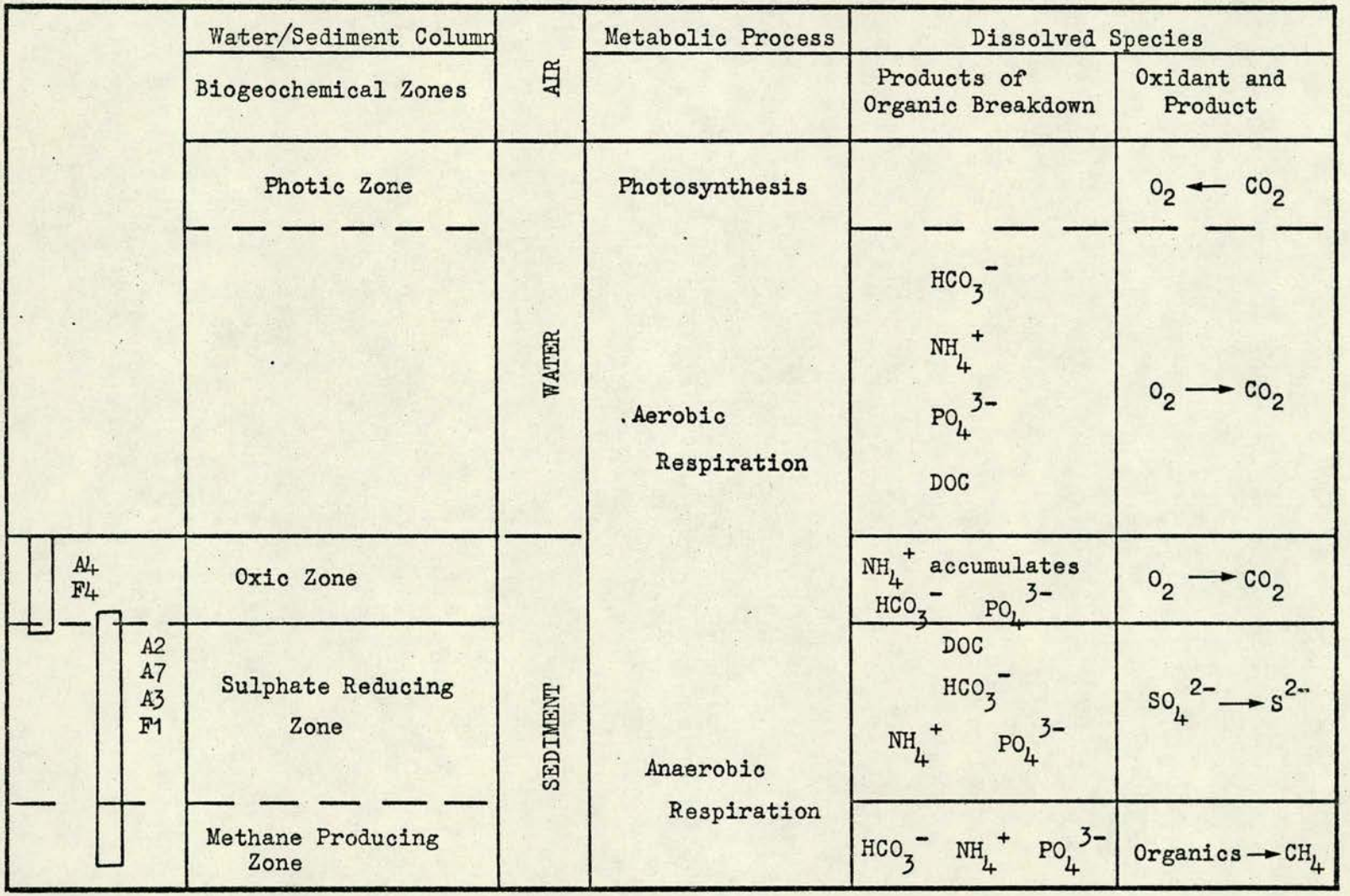


FIG. 5.1; Biogeochemical Zones Represented in the Sediments of Loch Duich (after Claypool and Kaplan 1974)

sequence of reactions that occur:

Organic species + oxidant ⟶ byproducts of organic breakdown + product of the oxidant reduced + free energy

The products are characteristic of the reactions which have occurred and are listed in Tables 5.I and 5 II.

Richards (1965) considered the reactions involved in aerobic respiration and anaerobic respiration, assuming nitrate and sulphate to be the oxidants. He used an average organic composition derived from data on living plankton of $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$. From this formula he calculated a series of equations for the byproducts of organic breakdown.

Aerobic respiration

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 \longrightarrow 106CO_2 + 106H_2O + 16NH_3 + H_3PO_4$$

Anaerobic respiration - Denitrification

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8HNO_3 \longrightarrow 106CO_2 + 148.4H_2O + 42.4N_2 + H_3PO_4 + 16NH_3$$

Anaerobic respiration - Sulphate reduction

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} \longrightarrow 106CO_2 + 106H_2O + 16NH_3 + H_3PO_4 + 53S^{2-}$$

Sholkovitz (1973) disagreed with the use of this stoichiometric ratio since it represents that of living plankton only, and not the organic matter found in sediment and therefore available for metabolic respiration. In both cases, although the stoichiometry in detail is different, the inorganic byproducts of organic breakdown are the same: HCO_3^-, NH_4^+ and PO_4^{3-}.

Table 5 I

Energy-yielding metabolic processes using glucose as the energy source under standard conditions (after Claypool and Kaplan 1974)

		kcal per mole of glucose equivalent oxidised
a	Aerobic Respiration	
	$CH_2O + O_2 \longrightarrow CO_2 + H_2O$	-686
b	Nitrate Reduction	
	$5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O$	-579
c	Sulphate Reduction	
	$2CH_2O + SO_4^{2-} \longrightarrow S^{2-} + 2CO_2 + H_2O$	-220
d	Carbonate Reduction	
	$2CH_2O \longrightarrow CO_2 + CH_4$	-99
e	Nitrogen Fixation	
	$3CH_2O + 2N_2 + 3H_2O \longrightarrow 4NH_3 + 3CO_2$	-57
f	Fermentation: heterolactic	
	Glucose $\longrightarrow$ Lactate + C_2H_5OH + CO_2	-49
g	Fermentation: Strickland reaction	
	Alanine + 2 Glycine + $2H_2O \longrightarrow$ 3 Acetate + CO_2 + $3NH_3$	-17

Table 5 II; Equilibrium Constants of the Principal Respiration Processes in Marine Conditions (after Stumm and Morgan 1970)

Metabolic reactions involving the transfer of one electron	$pE^{\circ}(=\log K)$	$pE^{\circ}(W)$
$\frac{1}{4} O_2(g) + H^+(w) + e = \frac{1}{2} H_2O$	+20.75	+13.75
$\frac{1}{5} NO_3^- + \frac{6}{5} H^+(w) + e = \frac{1}{10} N_2 + \frac{3}{5} H_2O$	+21.05	+12.65
$\frac{1}{2} MnO_2(s) + HCO_3^-(10^{-3}M) + \frac{3}{2} H^+ + e =$ $\frac{1}{2} MnCO_3(s) + \frac{3}{8} H_2O$		+8.50
$\frac{1}{2} NO_3^- + H^+(w) + e = \frac{1}{2} NO_2 + \frac{1}{2} H_2O$	+14.15	+7.15
$\frac{1}{8} NO_3^- + \frac{5}{4} H^+ + e = \frac{1}{8} NH_4^+ + \frac{3}{8} H_2O$	+14.90	+6.15
$FeOOH(s) + HCO_3^-(10^{-3}M) + 2H^+(w) + e =$ $FeCO_3(s) + 2H_2O$		-1.67
$\frac{1}{6} SO_4^{2-} + \frac{4}{5} H^+(w) + e = \frac{1}{6} S^0(s) + \frac{2}{3} H_2O$	+ 6.03	- 3.30
$\frac{1}{8} SO_4^{2-} + \frac{4}{5} H^+(w) + e = \frac{1}{8} H_2S(g) + \frac{1}{2} H_2O$	+ 5.75	- 3.50
$\frac{1}{8} SO_4^{2-} + \frac{9}{8} H^+(w) + e = \frac{1}{8} HS^- + \frac{1}{2} H_2O$	+ 4.13	- 3.75
$\frac{1}{8} CO_2^{2-} + H^+(w) + e = \frac{1}{8} CH_4(g) + \frac{1}{4} H_2O$	+ 2.87	- 4.13

Stumm and Morgan (1970) considered the same metabolic processes, basing their equilibrium constants on the principal redox reactions which occur in the marine environment. Table 5 II lists some of the more important of these reactions, the equilibrium constant of the reactions, and thus the sequence of biogeochemical zones.

In the marine environment the most important biogeochemical zones are:

a) the oxygen consuming aerobic zone

b) the sulphate reducing anaerobic zone and

c) the carbonate reducing - methane producing anaerobic zone.

Denitrification, the loss of nitrate and the build up of nitrite and nitrogen, has been observed in the water column of Saanich Inlet (Broenkow, 1963) and in the Cariaco trench (Richards and Benson, 1961) close to the boundary between the aerobic and anaerobic zones. Taylor (1974) has observed the changes from higher to lower oxidation states for iron and manganese close to the same boundary in several Norwegian fjords. These reactions are of secondary importance in controlling the chemistry, since the overall concentration of nitrate, Fe and Mn ions is low compared to that of oxygen and sulphate. Where these reactions have been observed, they confirm the validity of the sequence based on the thermodynamic values quoted in Tables 5 I and 5 II.

5.2 Position of the boundaries of the biogeochemical zones

Boundaries in the water column

The position of these boundaries within the water column depends on the availability and circulation of the oxidant. In a

freely circulating marine system any oxygen used in respiration is replaced from the photic zone or atmosphere. Any products of respiration are recycled back into the photic zone as nutrients. In environments where circulation in the bottom waters is restricted, the oxygen supply is exhausted; the Black Sea, the Cariaco trench and certain Norwegian and Canadian fjords are examples of such basins (Richards, 1965). They have restricted circulation, which results in semipermanent or permanent anoxic bottom-water conditions with associated sulphate reduction. In such basins a build-up of nutrients occurs.

In the coastal marine environment, the water column is typically entirely oxic. There is a high rate of organic productivity in the photic zone and, because of the relatively shallow depths of water, a high proportion of organic matter reaches the sediment. If the rate of sedimentation is sufficiently rapid, the detrital organic matter is buried before it is mineralised aerobically and then anaerobic respiration commences. Consequently, in such environments there is commonly a thin layer of aerobic-zone sediment underlain by a zone of sulphate reduction (see Figure 5 I); examples of such environments are Chesapeake Bay (Briggs, 1967), the Wadden Sea (Vosjan, 1974) and the California Borderlands (Emery and Rittenberg, 1952; Sholkovitz, 1973). The depth at which the boundary between the aerobic and anaerobic zones occurs is influenced by a number of factors; the degree of oxygen saturation of the overlying sea water; the porosity of the sediment, the rate of sedimentation, the nature of the organic input and bioturbation.

Each biogeochemical zone has a characteristic metabolic reaction

which makes use of different oxidants and occurs at a characteristic pE. During anaerobic respiration, there is also a build up of the products of organic decomposition; nutrients, sulphide, DOM. All of these variables can be used to recognise the zones and the dominant metabolic processes involved.

5.3 Chemical analysis of the pore waters

14 cores were collected on two successive trips to Loch Duich in April 1974 and February 1975. The location of the coring stations and the nomenclature of the cores are given in Figure 3.1. (For a discussion on the methods used in sampling, storage and analysis, see Appendix A and B.) The pore waters were analysed for titration alkalinity and sulphide on both trips, for sulphate on the pore waters collected in February 1975 and for phosphate on the pore waters collected in April 1974. The results of the chemical analysis of the pore water anions are given in Tables 5 III - V and in Figures 5.2 - 7.

Results: Chloride

Chlorinity is considered to be a conservative parameter in sediment pore waters unaffected by microbial action. Davies (1976) measured the chlorinity of a number of cores from Loch Duich including core A2. The method used was a silver nitrate titration with a chromate indicator. The results (Table 5 IV) show that there is a small (1 - 2%) lower value for the chlorinity as compared to that measured in the overlying sea water. Bischoff and Ku (1970) noted a lowering of chlorinity in pore waters collected from anoxic sediments in the Atlantic Ocean as compared to the overlying sea water by 1%,

Table 5 III

Chemical analysis of the concentration of the major pore water anions in cores A4 and F4, oxic cores from Loch Beg and the overlying sea water

Depth (cms)	Titration Alkalinity (meq/ltr)	Phosphate (μMol/ltr)	Sulphate (mMol/ltr)	Sulphide (mMol/ltr)
Core A4				
5	3.77	3.4		0.02
15	3.02	3.7		0.01
25	2.70	2.9		0
35	2.58	2.8		0
45	2.65	1.9		0.03
55	2.87	2.8		0.02
65	3.59	5.5		0.01
75	7.61	11.8		0.04
Core F4				
5	2.72		27.3	0.01
15	2.92		25.8	0.01
25	2.71		26.3	0.01
35	2.87		26.3	0
Sea Water				
	2.20		26.8	0
	2.18		26.0	
	2.19		27.1	

Table 5 IV

Chemical analysis of the concentration of the major pore water anions in cores F1 and A2, anoxic cores from station 1 in Loch Duich

Depth (cms)	Titration Alkalinity (meq/ltr)	Phosphate (μMol/ltr)	Sulphate (mMol/ltr)	Sulphide (mMol/ltr)	Chloride (grms/ltr)
Core F1					
5	3.88		27.6	0.01	19.20
15	7.89		26.0	0.01	18.88
25	16.69		17.8	0.07	18.89
35	26.12		13.4	0.68	18.95
45	32.94		6.4	2.19	18.91
55	40.66		0.2	2.88	18.95
65	44.12		0.7	1.85	18.89
75	52.53		0	0.77	18.92
84	56.81		0	0.52	18.91
Core A2					
5	7.16	19.8		0.02	
15	15.96	55.4		0.09	
25	24.54	55.9		0.29	
35	30.32	83.0		1.51	
45	40.02	107.4		1.87	
55	41.05	128.1		1.52	
65	49.31	189.5		0.87	
75	50.11	204.2		0.88	
85	52.41	224.7		-	

Table 5 V

Chemical analysis of the concentration of the major pore water anions in cores A7 and A3, anoxic cores from the central basin of Loch Duich

Depth (cms)	Titration Alkalinity (meq/ltr)	Phosphate (μMol/ltr)	Sulphate (mMol/ltr)	Sulphide (mMol/ltr)
Core A7				
5	7.72	32.6		0.02
15	15.46	32.7		0.04
25	25.86	17.5		0.33
35	35.58	118.1		1.22
45	41.01	122.9		1.71
55	45.36	122.3		2.09
65	49.37	151.7		1.42
75	53.31	207.6		0.66
85	56.91	-		0.30
Core A3				
5	-	24.3		
15	8.11	41.5		0.04
25	18.71	-		0.09
35	30.05	123.1		0.75
45	35.84	147.0		2.42
55	40.57	147.0		2.55
65	43.75	100.8		1.90
75	44.64	172.7		1.39

but were unable to explain it. Nissenbaum et al. (1972) observed a similar lowering in salinity in the pore waters collected from the sill of Saanich Inlet. They suggested that this may be due to a variation of the salinity of the fjord with time. There is no evidence either for or against this hypothesis of salinity variation in Loch Duich, and the answer is left open. The diagenetic changes of other anions are of an order of magnitude such that the 1 - 2% differences observed in the salt content of the pore waters are insignificant.

Vertical distribution of sulphate (Fig. 5.2)

The concentration of sulphate in pore waters was measured on cores F1A, F1B and F4 (Tables 5 III and IV). The values for the central cores (Figure 5.2) decrease from a concentration very close to that of sea water (27.6 mMoles/l) at the surface to zero at a depth of 50 - 60 cms. Below 50 cms there are a further thirty centimetres which are completely depleted in sulphate. Cores F1A and F1B, which were collected from adjacent cores, show a very close correspondence to one another. (For a discussion on the comparability in analysis of repeated sampling at the same station, see Appendix A.)

In contrast, core F4 , collected from Loch Beg, a bay at the head of Loch Duich, shows no significant depletion of sulphate throughout its length.

Murray and Irvine (1893) found a loss of sulphate in organic rich muds and an associated increase in alkalinity. Davies (1976) demonstrates that there is a change in the rate of increase of alkalinity from the depth in the core where sulphate is reduced to zero. A similar result was found in the pore waters of sediments from the

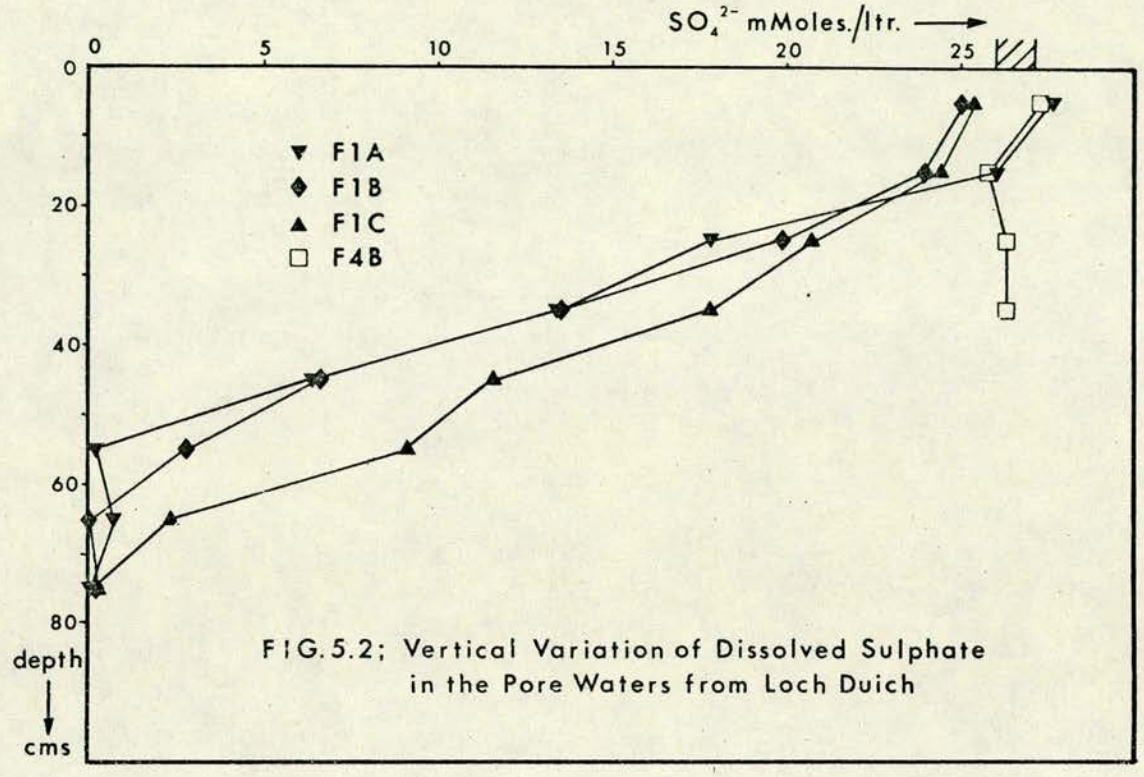


FIG. 5.2; Vertical Variation of Dissolved Sulphate in the Pore Waters from Loch Duich

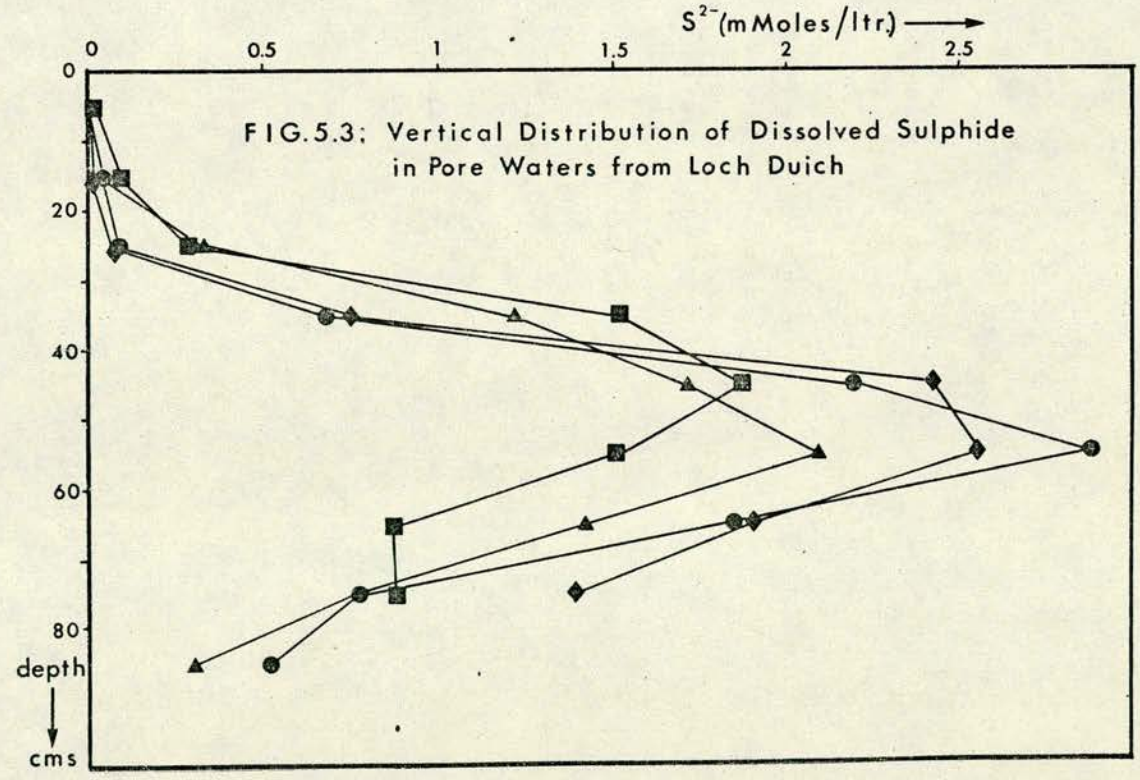


FIG. 5.3; Vertical Distribution of Dissolved Sulphide in Pore Waters from Loch Duich

South Guymas basin (Goldhaber, 1974).

Vertical distribution of sulphide (Fig. 5.3)

Sulphide is present in the pore waters of all the basin cores (Figure 5.3). The value increases from near zero at the surface of every core to a maximum of 1.9 - 2.9 mMoles/l and then falls to a value of 0.3 - 1.4 mMoles/l. The equilibrium concentration of sulphide at depth is not known from this study, since the concentration of sulphide was still dropping at the lowest sampled point in each core. In core F1A and F1B, where sulphide and sulphate were analysed on the same pore water sample, the maximum value for sulphide coincides with the depth where sulphate becomes depleted. A similar observation was made by Nissenbaum et al. (1972) and Goldhaber and Kaplan (1974, 1975). This was due to the uptake of sulphide produced during sulphate reduction, by solids, principally iron oxides, within the sediment. While sulphate reduction occurred, there was a surplus of free sulphide which accumulated in the pore waters; when sulphate became depleted, no further sulphide was produced and the concentration of free sulphide in the pore waters decreased. The maximum value of sulphide is taken as the depth at which sulphate reduction ceases.

The cores from Loch Beg show only traces of sulphide (0.01 - 0.04 mMoles/l).

Vertical distribution of phosphate (Fig. 5.4)

The results from the basin cores show an accumulation of phosphate throughout the zones of anaerobic respiration from a value of 35 - 40 µMoles/l at the surface to 180 - 240 µMoles/l at the deepest layer sampled.

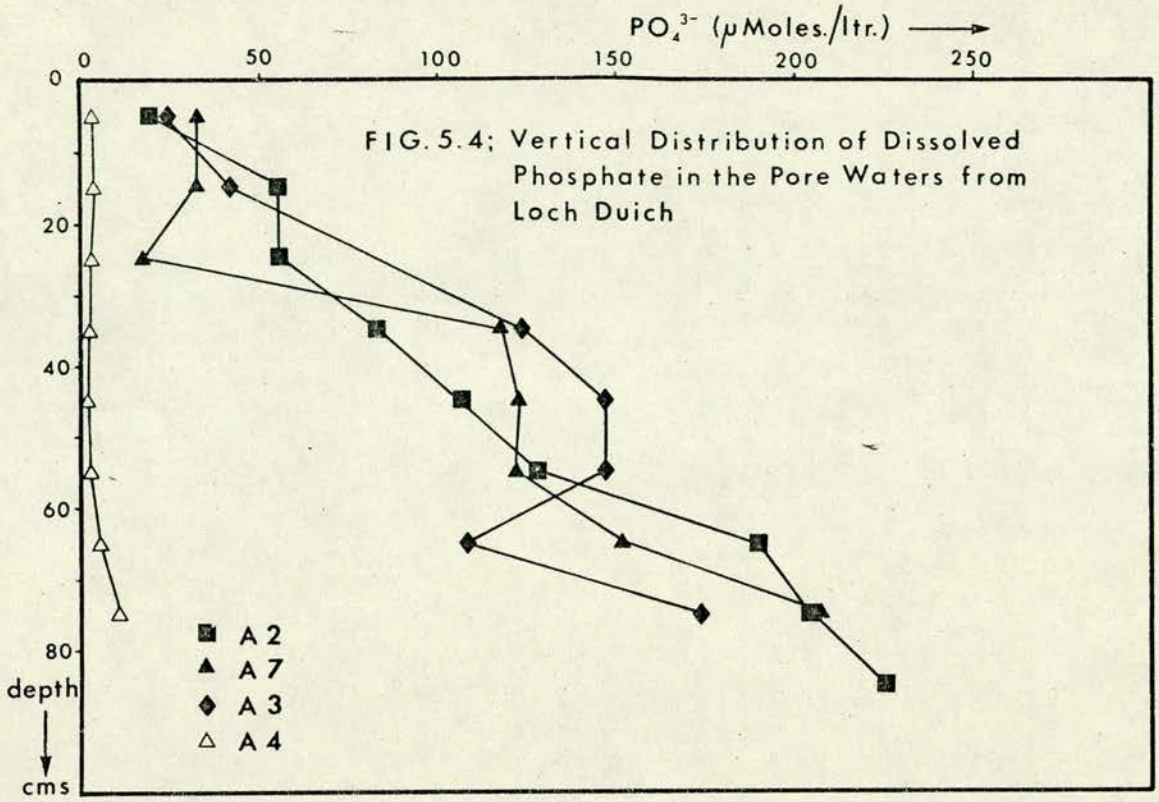


FIG. 5.4; Vertical Distribution of Dissolved Phosphate in the Pore Waters from Loch Duich

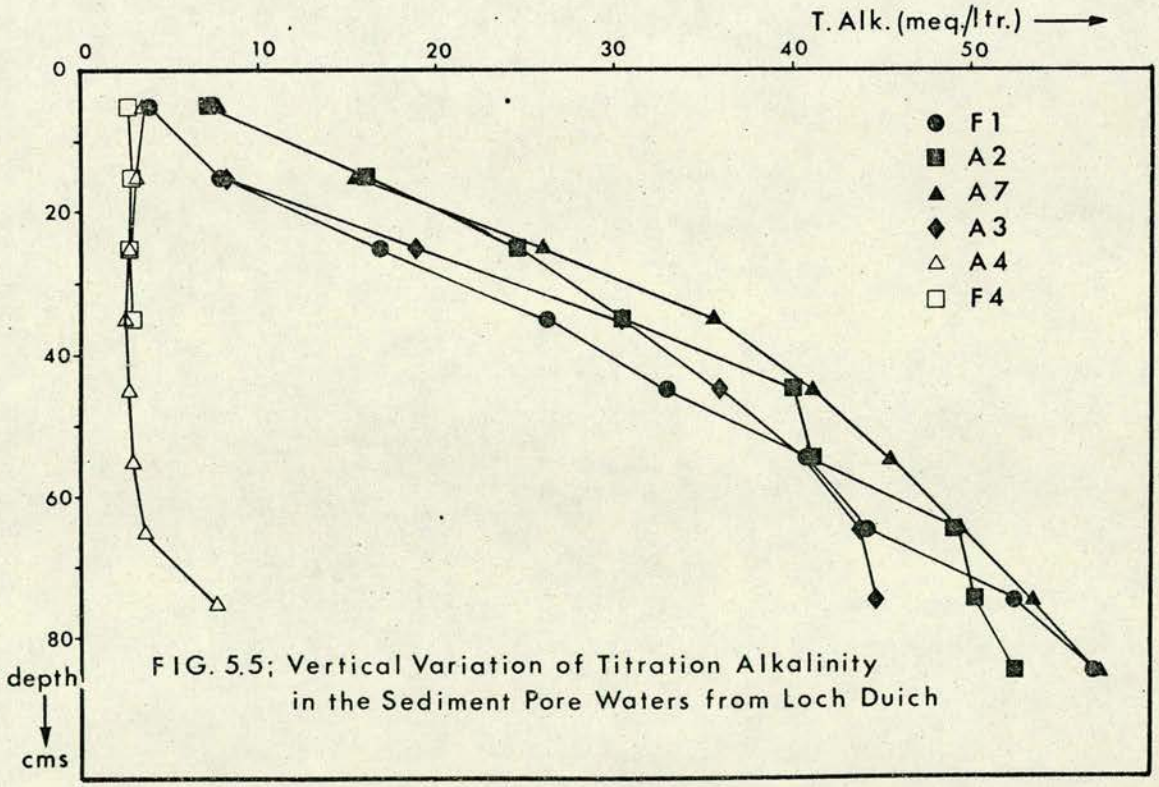


FIG. 5.5; Vertical Variation of Titration Alkalinity in the Sediment Pore Waters from Loch Duich

The increase, though somewhat erratic, showed that the accumulation of phosphate correlated well with that of titration alkalinity particularly within the zone where sulphate reduction was active. Below this zone alkalinity accumulated within the pore waters faster than phosphate did, a result confirmed by the analyses of Davies (1976), Sholkovitz (1973) and Hartmann et al. (1973).

It has been noted that the accumulation of phosphate correlated not only with titration alkalinity but also with ammonia (Rittenberg et al., 1955; Presley and Kaplan, 1968 and Sholkovitz, 1973). For a more complete discussion of the relationship between phosphate, ammonia and alkalinity in the pore waters of Loch Duich, see Davies (1976).

In contrast to the pore waters from the basin cores, the phosphate concentration in core A4 was very low (3 μMoles/l). There was a slight increase in the lowest two depths to 5 and 11 μMoles/l. It is suggested that this was the depth at which sulphate reduction was commencing.

Vertical distribution of titration alkalinity (Fig. 5.5)

Titration alkalinity increased with depth in the basin cores. The surface values were slightly above that of the overlying sea water (2.20 meq/ltr); the excess alkalinity was used as a measure of the length of core missing due to the splash effect of the gravity corer (3 - 7 cms) (see Appendix A). The alkalinity increased to a value of 40 - 45 meq/ltr at the depth where sulphate became totally depleted. This portion of the curve showed a linear increase with depth and a direct correspondence with phosphate accumulation and sulphate depletion (Figure 5.6). A similar relationship was found

in the sediments of the California borderlands (Presley and Kaplan, 1968; Sholkovitz, 1973), in the sill sediments of Saanich Inlet (Nissenbaum et al., 1972) and in Somes Sound, Maine (Berner et al., 1970).

In cores F1 and A2, the maximum value for the sulphide concentration coincides with the change of gradient of the graph of titration alkalinity against depth. This relationship was also shown in the data of Nissenbaum et al. (1972), Berner et al. (1970) and Goldhaber and Kaplan (1974). These results emphasise the ubiquity of these patterns of anion relationship in the pore waters of shallow coastal marine sediments.

The titration alkalinity of cores from Loch Beg shows relatively minor changes with depth. There is a small excess (0.5 - 1.6 meq/ltr) above that found in the overlying sea water. Below 50 cms in core A4 there is an increase in alkalinity from 2.9 meq/ltr at A4A40 to 7.6 meq/ltr at A7A70, which was due to the commencement of sulphate reduction within the sediment. Above 50 cms it was not possible to decide from the data collected whether the slight increase in alkalinity, traces of sulphide and minor depletion in sulphate were due to small pockets of local sulphate reduction within an overall oxic environment or to diffusion of anions from the zone of sulphate reduction below.

5.4 Discussion

The measurement of titration alkalinity, sulphate and sulphide enabled the metabolic zones found in the sediment interstitial waters of Loch Duich and Loch Beg to be fully defined (Figure 5.6). The

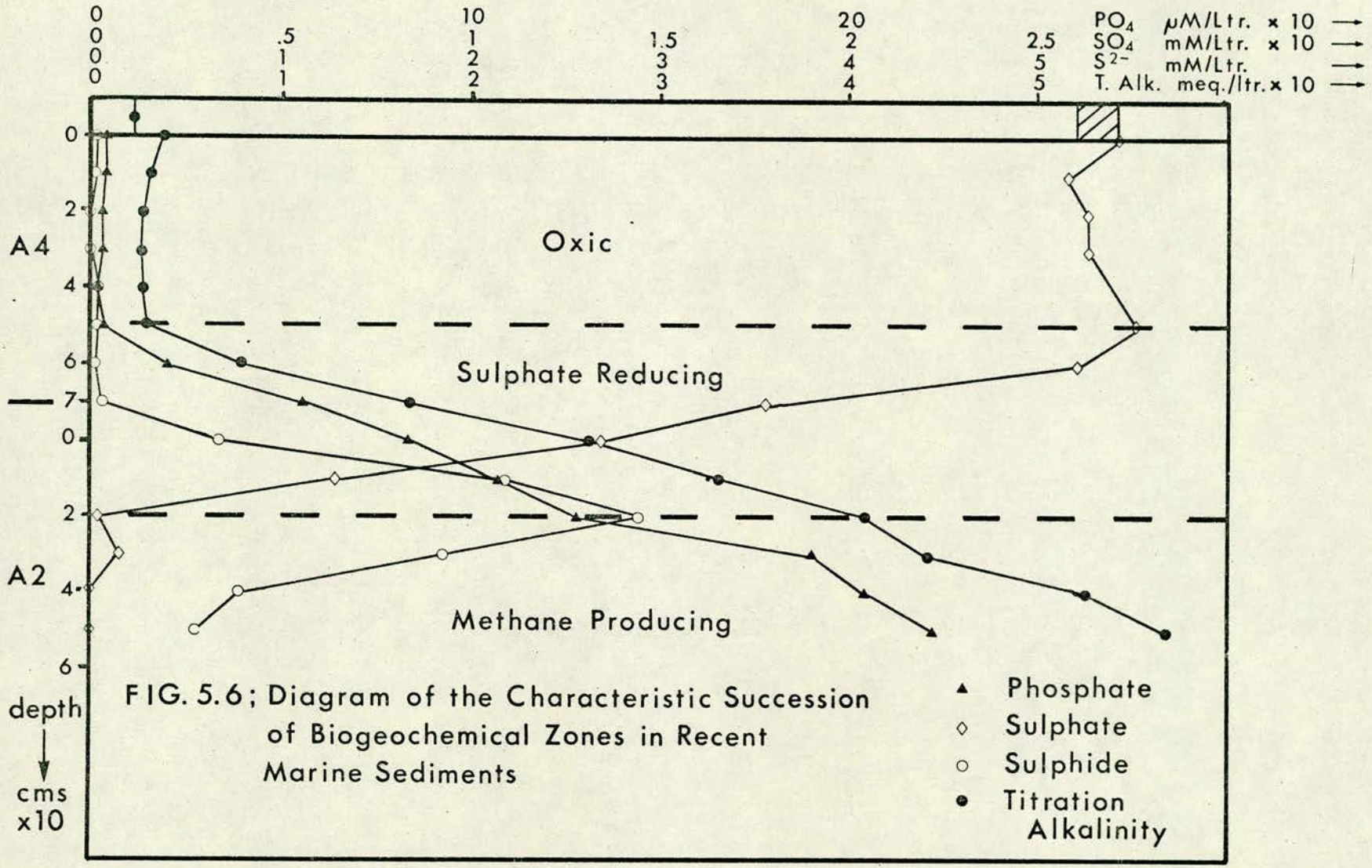


FIG. 5.6; Diagram of the Characteristic Succession of Biogeochemical Zones in Recent Marine Sediments

cores sampled from Loch Beg were interpreted as being within the oxic biogeochemical zone. They showed no significant change in the concentration of pore water anions from that found in the overlying sea water. The boundary between the oxic zone and the zone of sulphate reduction occurred at a depth of 60 - 70 cms in core A4. Below this, there was evidence of sulphate reduction; an increase in titration alkalinity and an accumulation of phosphate and sulphide. The portion of the basin cores in which there was a linear decrease in sulphate and an accumulation of alkalinity, sulphide and, by inference, phosphate and ammonia is defined as the zone of sulphate reduction. Below this zone, the sulphate became totally depleted, the rate of increase in the accumulation of titration alkalinity was reduced and the concentration of sulphide found in the pore waters decreased. Reeburgh (1969) analysed dissolved sulphate and methane in anoxic sediments from Chesapeake Bay. The results showed an increase in methane occurs after complete depletion of sulphate. This result was confirmed by Martens and Berner (1974). From this work it is suggested that the zone below the depth of total sulphate depletion where there was a continued increase in titration alkalinity and accumulation of phosphate (and ammonia) is the zone of carbonate reduction and methane production (Claypool and Kaplan, 1974). The boundary between the zone of sulphate reduction and the zone of methane production is defined by complete sulphate depletion, a change in the gradient of the alkalinity curve and the maximum value for sulphide.

Each biogeochemical zone has a characteristic pattern of changes in pore water anions. These patterns have been identified in a

number of shallow coastal marine environments such as the California borderlands (Rittenberg et al., 1955; Sholkovitz, 1973), Chesapeake Bay (Briggs, 1967; Reeburgh, 1969), the Wadden Sea (Vosjan, 1974) and Somes Sound (Berner et al., 1970) as well as in Loch Duich. For a more detailed discussion on models for the diagenesis of organic matter, particularly in the zone of sulphate reduction, as they affect the concentration of pore water anions, the reader is referred to Sholkovitz (1973), Hartmann et al. (1973) and Davies (1976). In this study, the diagenesis of organic matter and trace metals is related to these biogeochemical zones and thus the results are applicable to other shallow coastal marine sediments.

Loch Beg sediments as oxic sediments

Although the sediments of Loch Beg have the characteristic pore water geochemistry of oxic sediments; similar levels of phosphate and alkalinity as the overlying sea water and little or no sulphate depletion (Shishkina, 1964; Rittenberg et al., 1955), it is necessary to explain the lack of any significant sulphate reduction to a depth of 60 centimetres despite the presence of a high concentration of total organic carbon (5.8%). Loch Beg sediments are not reducing either because (1) organic breakdown is occurring and the nutrients which form are then rapidly recycled back to the overlying sea water, or (2) that nutrients are not produced because the organic matter is unreactive.

There is evidence from the C/N and I/C ratios in the sediment (Chapter 7.4) that decomposition of organic matter is occurring in the Loch Beg sediments. There is an increase in C/N ratio from 14.2 - 14.6 at the surface to 16.4 - 16.7 at depth in the sediment, while

there is no recognisable trend in the C/P ratio with depth. Thus N, probably in the form of NH_4^+, is being released into the pore waters, whereas P is not released throughout most of the core. Note that there is an accumulation of NH_4^+ but not of PO_4^{3-} ions found in the fully marine oxic sediments of the Santa Monica basin, California (Rittenberg et al., 1955). In addition there is a significant decrease in the I/C ratio from 21.7 - 37.1 at the surface to 7.1 - 12.9 at depth in the Loch Beg sediments and thus it is inferred that I is released from the sediment into the pore waters, a similar release of I from both oxic and anoxic sediments has been noted previously (Price and Calvert, 1973a).

A high rate of exchange between the sediment interstitial waters and the overlying sea water may be caused by bioturbation. Although bioturbation occurs in sediments down to abyssal depths, the greatest activity in terms of number of burrowing organisms and probably also sediment turnover occurs in sediment present in water depths of less than 20 metres (Schafer, 1972). However, although bioturbation commonly affects sediment to a depth of approximately 30 cms, it is considered unlikely that biological turnover could still affect a sediment to a depth of 60 cms and thus bioturbation can only provide a partial explanation for the thickness of oxic sediment found in Loch Beg.

Particularly at depths of 30 - 60 cms within the sediment, diffusion is possibly an important process in keeping the pore waters oxygenated and recycling the products of respiration. Loch Beg sediments have a greater available porosity than the basin cores, and thus diffusion of any dissolved species within the pore waters is

more rapid.

The oxicity of deep oceanic sediments is due mainly to the unreactivity of the organic matter that reaches the sediment (Shishkina, 1963). Most of the sediments and organic matter in Loch Beg are derived directly from the River Croe and are terrestrial in origin. Little is known about the reactivity of terrestrial organic matter in the marine environment. Cellulose effluent from a pulp mill near Fort William appears to be resistant to microbial breakdown in the oxic marine environment but breaks down rapidly in anoxic sediments (S. Stanley, pers. comm.)

However, the quantitative effects of bioturbation, the rate of diffusion, the sedimentation rate and the reactivity of terrestrial organic matter in the marine environment are all unknown for the sediments of Loch Duich and Loch Beg, and hence it is not possible to separate the relative importance of these factors in explaining the observed lack of sulphate reduction in the Loch Beg sediments.

CHAPTER 6

DISSOLVED ORGANIC MATTER IN THE PORE WATERS

6.1 Introduction

During the diagenesis of organic matter within the sediment, not only is a proportion mineralised to form nutrients (HCO_3^-, NH_4^+, PO_4^{3-}), but a fraction is solubilised to form dissolved organic matter (DOM) (Otsuki and Hanya, 1972a+b). Although there have been a number of studies on the accumulation of nutrients within sedimentary pore waters (Rittenberg et al., 1955; Sholkovitz, 1973; Hartmann et al., 1973), there have been very few studies which have investigated the nature and changes of DOM in marine sediment pore waters (Nissenbaum et al., 1971).

The pore waters of the sediments from Loch Duich are yellow in colour, similar to those of Saanich Inlet (Brown et al., 1972). This yellow colour seemed to be related to the extent of reduction that had occurred within the sediment. The pore waters from Loch Beg cores and the top of the basin cores were pale in colour, the yellowness as measured by light absorbance at 420 nm.[1] increasing with depth (Figure 6.1).

The only previous study on the DOM from sediment interstitial

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[1] This absorbance is known to be proportional to yellow colour as measured against chloroplatinate standards (Black and Christman, 1963).

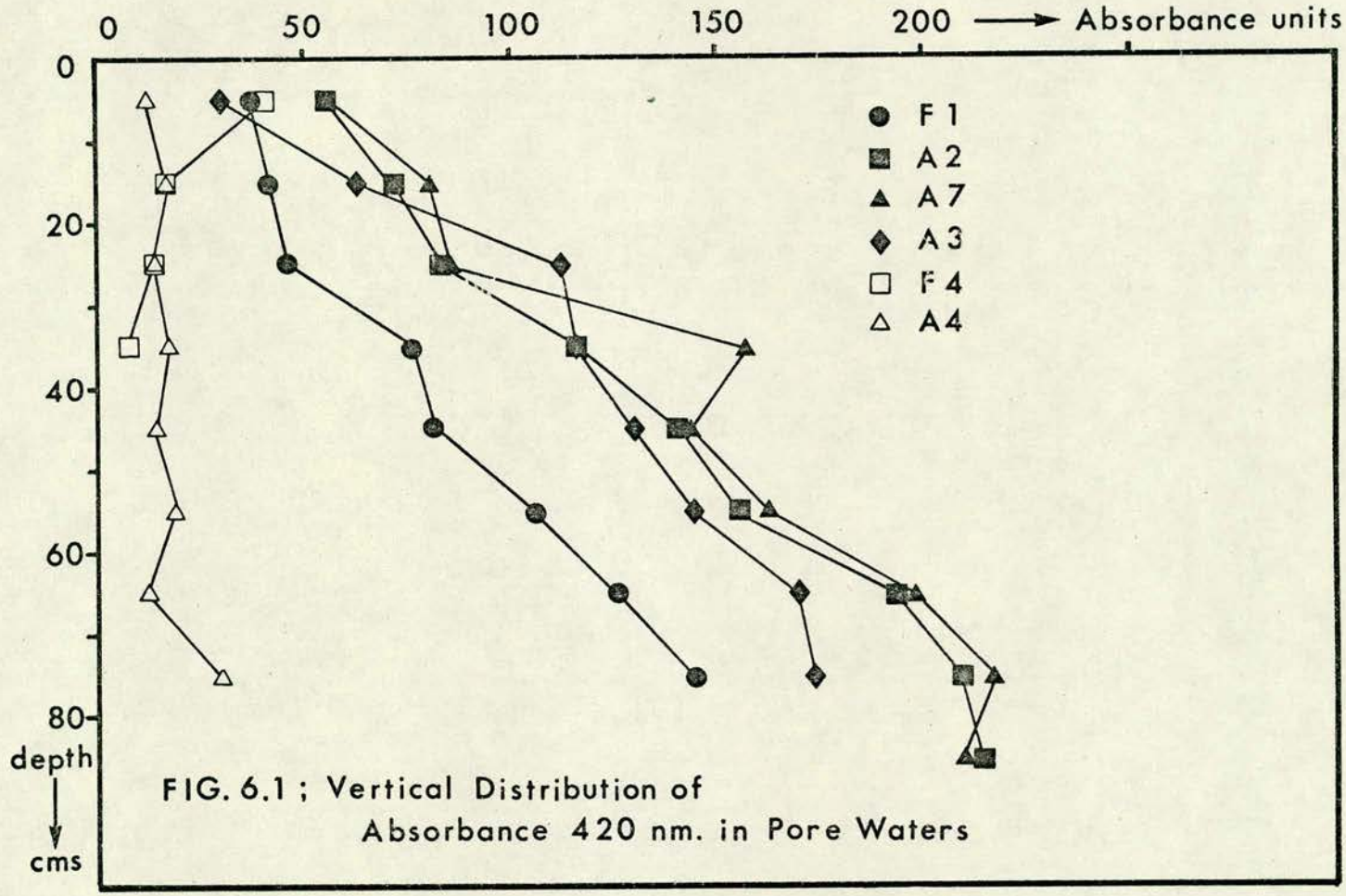

FIG. 6.1 ; Vertical Distribution of Absorbance 420 nm. in Pore Waters

waters was conducted by Nissenbaum et al. (1971) on pore waters from Saanich Inlet. They showed that the concentration of organic matter in pore waters is an order of magnitude greater than that in the overlying sea water. In addition, the change of concentration of DOC with depth was investigated. As in this study on Loch Duich, a molecular weight separation of organics into two fractions was performed and the high molecular weight fraction analysed for its elemental composition, its organic composition and its variation with depth. Unfortunately, because of the lack of sufficient data points in the cores collected from Saanich Inlet, it was not possible to draw anything more than tentative conclusions about the nature of DOM in sediment interstitial waters and the processes involved in its production and accumulation. The following study is an attempt at a more comprehensive and systematic study of this problem.

In this study, the elemental composition of the dissolved organic matter is identified using spectroscopic and chemical techniques. In particular, it was hoped that this knowledge might be used to explain the observed behaviour of certain trace metals (Mn, Fe, Cu and Zn) in sediment interstitial waters. It was also hoped to identify changes in DOM profiles with depth, to relate these to the biogeochemical zones and hence provide some interpretation of the metabolic processes which control the DOM in pore waters.

Previous research on DOM in sea water has involved concentrating the organics by chemical or physical techniques, such as absorption on activated charcoal (Kerr and Quinn, 1975), on a nylon column (Sieburth and Jensen, 1968) or separation at the boundary of an emulsion Khailov, 1968). These techniques tend to have only partial

recoveries, and there is no information available as to whether the organic matter separated is representative of the organic matter as a whole. Such separation techniques were not necessary in the pore waters of Loch Duich because of the high concentrations of organics present.

In addition to measurements on untreated pore waters, a separation was performed using membrane ultrafiltration to divide the DOM into two fractions: a high molecular weight fraction (M.W. > 1000) and a low molecular weight fraction (M.W. < 1000). The elemental concentrations of carbon and trace metals were measured for both these fractions to investigate the molecular weight partitioning of DOM in pore waters and the relative distribution of trace metal. An acid-insoluble fraction was found to appear on storage of pore waters at pH = 2; it was investigated initially to determine whether it affected the analysis of trace metals. It was found to be a humic acid precipitate and gave information on the partitioning of the "humic"[1] material in the pore waters between humic acid and

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[1] "Humic" material is defined here as any yellow-coloured organic matter found in the pore waters. No attempt is made by the use of this term to differentiate between Humic, Fulvic and Hymatomelanic acids as defined by Packham (1964). The term Gelbstoff (Kalle, 1966) is closely analogous. He applied it to yellow material in sea water. This specific term has not been used in this study, so as to avoid any implication that the yellow organics in pore waters are a priori derived from, or chemically similar to the yellow organics found in sea water.

fulvic acid and also on the elemental composition of the humic acid fraction of the DOM.

The techniques of analysis and the standard classification applied to "humic" substances (Schnitzer and Kahn, 1972) are particularly well suited for work on the DOM in sediment pore waters. Both marine and soil organic matter are derived from plant material which has been decomposed by microbial action and then condensed and polymerised to form high molecular weight, often yellow coloured, organic molecules which contain within their structure derivatives of many of the common molecules (amino acids, carbohydrates, fatty acids, etc.) found in living tissues. It must be noted, however, that by using a similar classification system to that of the soil scientist, a division into humic, fulvic and hymatomelanic acids (Schnitzer and Kahn, 1972; Packham, 1964), the similarities of properties are emphasised and the differences minimised.

UV and visible spectroscopy was used to give qualitative and quantitative data on the organics in untreated pore waters, while IR spectroscopy was used to characterise the acid-insoluble precipitate.

A series of experiments was performed to test the use of light absorbance as a quantitative measure for DOC in sediment pore waters. The values of absorbance of DOM were calibrated against a series of DOC values obtained by a dry combustion technique. The optimum conditions of wavelength and pH were determined. DOC concentrations, as determined both directly by a combustion method (Gordon and Sutcliffe, 1973) and by the non-destructive spectroscopic method, were used throughout to give a quantitative measure of the DOM. Attempts were also made to measure dissolved organic phosphorus (DOP) and

dissolved organic nitrogen (DON). However, problems were encountered with these analyses because of the high background level of mineralised components (NH_4^+ and PO_4^{3-} present in the pore waters. Trace metals were also analysed and the results obtained were related to the possible presence of trace metal - organic complexes and chelates (Chapter 8). Figure B.1 represents a flow diagram for the scheme of analysis associated with DOM, the details of the methods are set out in Appendix B.

6.2 UV spectroscopy

These methods are attractive because they a) are non-destructive, b) are experimentally simple and c) provide valuable information on molecular structure and chemical interactions of DOM in pore waters. The UV and visible spectrum of the untreated pore waters from 660-210 nm was examined both as a continuous spectrum and as a series of absorbances at specific wavelengths. These measurements helped to identify qualitatively the nature and relative changes in the concentration of the various organic fractions present.

The continuous spectrum (Figure 6.3) shows a gradual increase of absorbance with decreasing wavelength at the visible end of the spectrum (600-400 nm); the increase becomes progressively greater at lower wavelengths (400-210 nm). This spectrum was similar to that characteristic of "humic" material (Schnitzer and Kahn, 1972). The only distinctive feature of the curve is a weak "shoulder" between 250 and 275 nm. This shoulder was absent in the freshwater humics of Shapiro (1957), but has been observed in marine Gelbstoff (Kalle, 1966), the exudate of algae (Akiyama, 1971) and the reducing pore

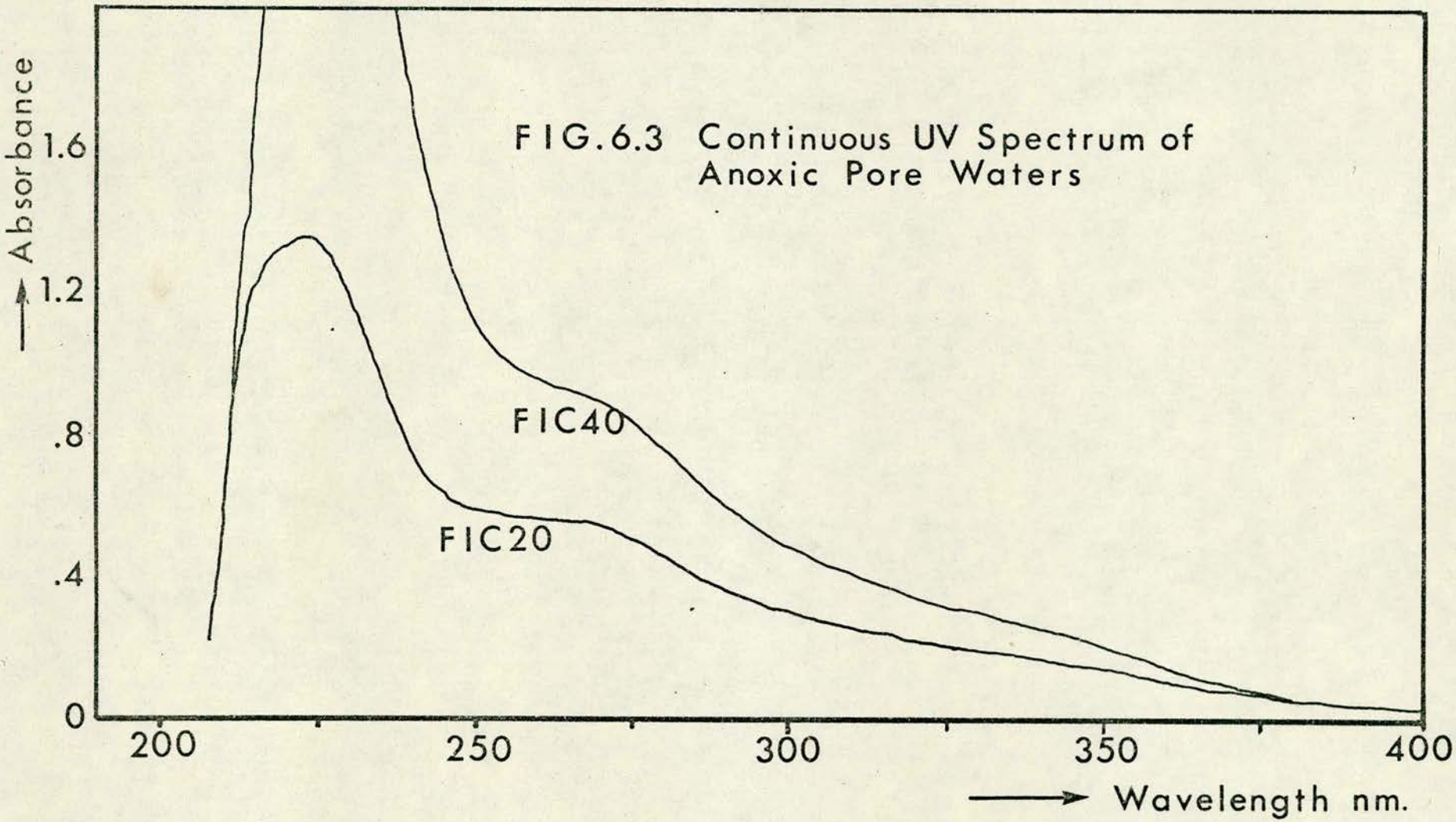

FIG. 6.3 Continuous UV Spectrum of Anoxic Pore Waters

waters from Saanich Inlet (Nissenbaum et al., 1971).

Spectral ratio

The ratio of optical densities or absorbances at 420 nm and 620 nm[1] (E_4/E_6) is used to identify and characterise "humic" substances (Schnitzer and Kahn, 1972).

All humic substances have a similar absorption spectrum (Figure 6.3), but the relative rate of change of absorbance with wavelength is a characteristic property of different "humic" substances; the ratio of absorbances (spectral ratio) is a measure of this gradient. The choice of wavelengths is arbitrary, 420 nm and 620 nm are used because these wavelengths are conveniently placed within the spectrum measurable on an optical spectroscopy. Because of the restriction on the volume of pore waters available in this study, the absorbance at 620 nm was low and somewhat unreliable. The ratio of absorbances at 360 nm and 420 nm (E_3/E_4) was therefore used to give an additional measure of the change of the spectral ratio with depth. The semi-quantitative value of E_4/E_6 was used to identify the nature of the "humic" fraction in solution by comparison with the results of other investigations.

The values for E_4/E_6 and E_3/E_4 for a number of the reducing cores (Table 6 I and Figs. 6.4 and 6.5) show that there is a general increase in spectral ratio with depth. For the analytical reasons explained above, the increase is more regular for E_3/E_4, but is

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[1] The ratio of absorbances at 465 nm and 665 nm is also commonly used as an alternative spectral ratio.

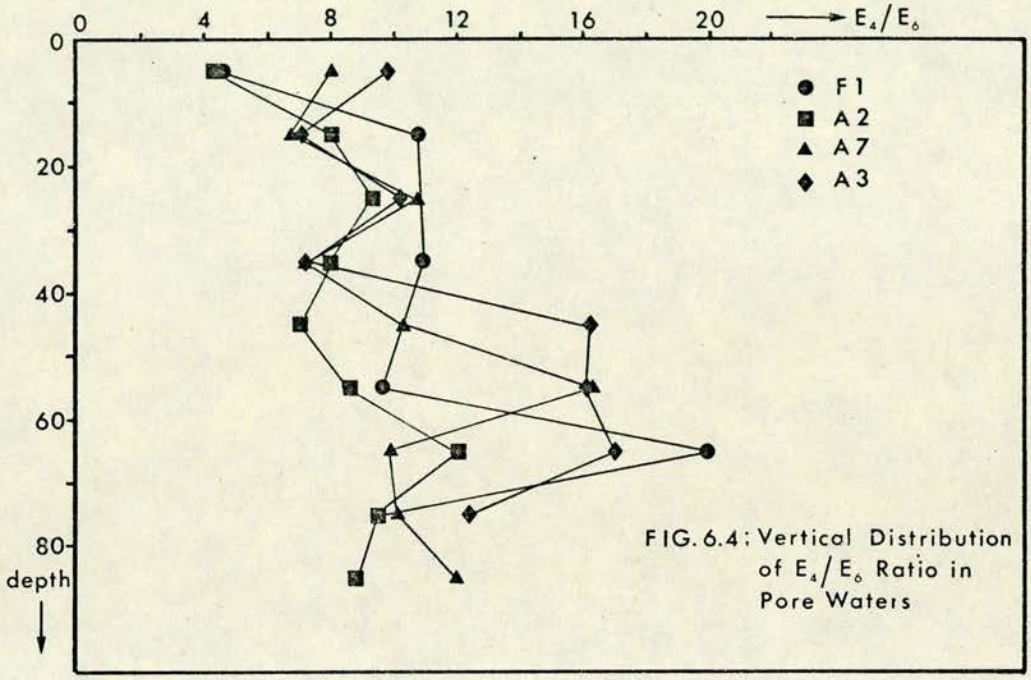

FIG. 6.4: Vertical Distribution of E_4/E_6 Ratio in Pore Waters

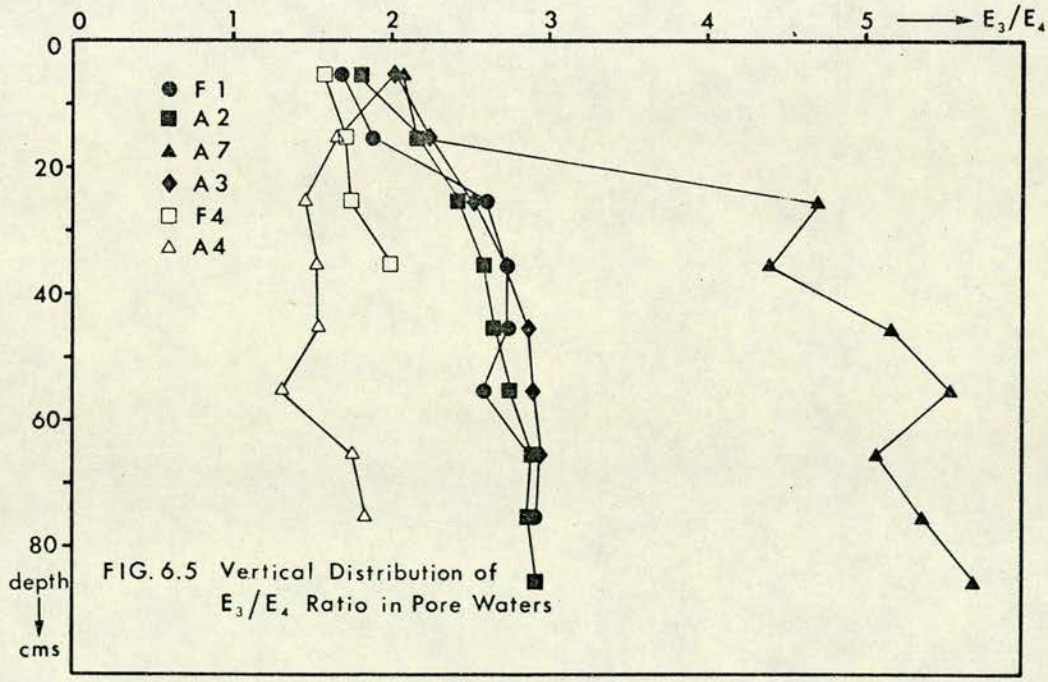

FIG. 6.5 Vertical Distribution of E_3/E_4 Ratio in Pore Waters

Table 6 I

The vertical distribution of spectral ratios, E_4/E_6 and E_3/E_4 for anoxic (F1, A2, A7 and A3) and oxic (F4 and A4) cores

Core and depth		E_3/E_4	E_4/E_6	Core and depth		E_3/E_4	E_4/E_6
A7	5	2.07	8.0	A2	5	1.80	4.31
	15	2.17	6.75		15	2.18	8.0
	25	4.70	10.75		25	2.43	9.33
	35	4.39	7.18		35	2.59	8.0
	45	5.17	10.29		45	2.66	7.05
	55	5.55	16.3		55	2.76	8.61
	65	5.08	9.9		65	2.90	12.13
	75	5.38	10.12		75	2.87	9.5
	85	5.70	12.0		85	2.92	8.9
A3	5	2.03	9.83	F1	5	1.68	4.56
	15	2.24	7.0		15	1.88	10.75
	25	2.52	10.23		25	2.60	-
	35	2.72	7.25		35	2.74	10.92
	45	2.88	16.19		45	2.75	36.5
	55	2.90	16.11		55	2.60	9.64
	65	2.96	17.0		65	2.89	19.9
	75	2.93	12.42		75	2.92	9.6
A4	5	2.0	-	F4	5	1.6	3.5
	15	1.63	8.0		15	1.7	-
	25	1.43	7.0		25	1.75	-
	35	1.54	3.2		35	2.0	-
	45	1.55	3.6				
	55	1.32	3.2				
	65	1.77	13.0				
	75	1.85	7.5				

definitely visible in E_4/E_6 as well. Soil humic acids show an increase in spectral ratio which is interpreted as being caused by a progressive increase in condensation and humification (Schnitzer and Kahn, 1972). However, it is not possible to generalise this observation to fulvic acids in soils, because insufficient work has been done. The E_4/E_6 ratio for humic substances, isolated from marine sediments, does not correlate in any simple way with the C/H ratio (Nissenbaum et al., 1971); thus there is no simple relationship between spectral ratio and the condensation of the "humic" material whose spectrum is being measured.

The magnitude of E_4/E_6 for the "humic" material in the reducing pore waters ranges from 6.75 to 17.0 with a mean value of 10.4. Despite the considerable scatter of these values as well as the trend noted above, the mean value for the spectral ratio is clearly closer to the range of fulvic acids (8.48-9.04) and above the typical range of E_4/E_6 found for humic acids (5.02-7.43) (Table 6 II). Thus it is concluded that the bulk of the "humic" material found in reducing pore waters is fulvic acid rather than humic acid. This is confirmed by measurements on acidified pore waters in which the humic acid has been removed by precipitation. This acid insoluble humic acid precipitate was weighed and found to represent approximately 1% of the total DOM, while measurements of absorbance (280 nm) before and after acidification showed no systematic difference.

Values of E_4/E_6 greater than 10 are higher than those found previously by other workers for fulvic and humic acids and implies that there is another fraction present which causes this higher ratio. Kalle (1966) measured E_{420}/E_{665} for a series of Gelbstoff solutions,

Table 6 II

Comparison of E_4/E_6 spectral ratios for fulvic (FA) and humic (HA) acids derived from various sources

Source	Fraction	E_4/E_6	Reference
Fucus	HA	5.97	Rashid and Prakash (1972)
	FA	9.04	
Laminaria	HA	5.26	
	FA	8.86	
	Algal Exudate	12.09	
River water	FA	9.04	
San Pedro sediments	HA	5.20	Nissenbaum and Kaplan (1971)
	FA	8.48	
Long Basin sediments	HA	7.43	
	FA	8.94	
Soils	HA	3.0 - 5.0	Schnitzer and Kahn (1972)
	FA	6.0 - 8.5	
Loch Duich anoxic pore waters	DOM	6.75-17.0	This study

but because of the spectral ratio used, the magnitude of the values cannot be directly compared with the E_4/E_6 ratio of other workers. The highest spectral ratios measured were melanoidins[1] with lower ratios for fulvic and humic acids. The E_4/E_6 ratio was also measured for the exudate of decomposing algae, which has been suggested as a precursor to both Gelbstoff in sea water (Rashid and Prakash, 1972; Sieburth and Jensen, 1968a,b) and to humic acids in marine sediments (Nissenbaum et al., 1971). The ratio of 12 for this algal exudate was also greater than that found for fulvic acids. Thus the high value for E_4/E_6 ratio observed in reducing pore waters was due to (1) a high ratio of fulvic to humic acid and (2) the presence of an unknown amount of a chemical fraction showing the spectral ratio characteristic of the exudate from algae and possibly chemically similar to a "melanoidin". The observed increase in spectral ratio represents a change in the relative proportions of melanoidin, fulvic and humic acids.

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[1] Melanoidins, first described by Maillard (1912) are dark coloured, amorphous, nitrogen-containing condensation products of amino acids and reducing sugars. The structure has not yet been established. "Standard" melanoidin has a molecular weight of 1478 and a colour and array of functional groups similar to those of humic acids, for which it has been suggested as a precursor. For a further discussion on Melanoidins, the reader is referred to Manskaya and Drozdova (1968) (pp. 58-79).

6.3 Total dissolved organic carbon (DOC) (Table 6 VI)

The vertical distribution of total DOC as measured by dry combustion (Gordon and Sutcliffe, 1973) in the interstitial waters of Loch Duich sediments is shown in Figure 6.6. DOC increases with depth in the reducing cores from a surface value (11.9 - 16.8 mg/litre) close to that of the overlying sea water in the core liner (6.7 mg/litre) to a value of 39.4 - 65.9 mg/litre at a depth of 75 cms. It is relatively unaffected by the transition from sulphate-reducing to methane-producing zones. In the oxic core A4 there was a low and fairly constant value of DOC (8.3 - 12.3 mg/litre), which showed no systematic variation with depth, but which was significantly higher than the value for the overlying sea water (5.1 mg/litre). Core F4 has an anomalously high surface DOC concentration (20 mg/litre), while the subsurface distribution was similar to that observed in core A4.

Use of light absorbance as a quantitative measure of organic matter in sediment interstitial waters

A series of experiments was carried out to test the conditions of pH and wavelength in which absorbance can be used to measure DOC in sediment pore waters. In previous studies using absorbance as a quantitative measure of DOC it was noted that the standards used must be of a similar origin to that of the unknowns (Schnitzer and Kahn, 1972). In this study the absorbance was calibrated using values for DOC obtained by dry combustion.

Effect of pH on absorbance

Shapiro (1957) and Sieburth and Jensen (1968a) note that the absorbance of solutions of "humic" substances from different origins

Table 6 VI

Concentration of total DOC in the pore waters

Core and depth (cms)		DOC (mg/ltr)	Core and depth (cms)		DOC (mg/ltr)
A2	5	16.8	A4	5	9.2
	15	22.4		15	10.6
	25	25.2		25	12.3
	35			35	8.3
	45	38.4		45	10.7
	55			55	9.5
	65			65	
	75	55.9		75	
A7	5		Sea water		6.1
	15	24.2	"		6.7
	25	29.4	"		6.7
	35	34.6	"		5.1
	45	42.2			
	55	43.6			
	65	48.5			
	75	70.5			

Core and depth (cms)		LMW fraction	HMW fraction	DOC
F1	5	6.0	7.6	13.6
	15	10.0	8.4	18.4
	25	11.5	9.8	21.3
	35	8.1	22.3	30.4
	45	9.8	22.7	32.5
	55	10.7	31.8	42.5
	65	13.2	40.1	53.3
	75	14.7	55.2	69.9
F4	5	8.3	7.5	15.8
	15	8.1	2.2	10.3
	25	10.4	5.4	15.8
	35	9.4	4.2	13.6

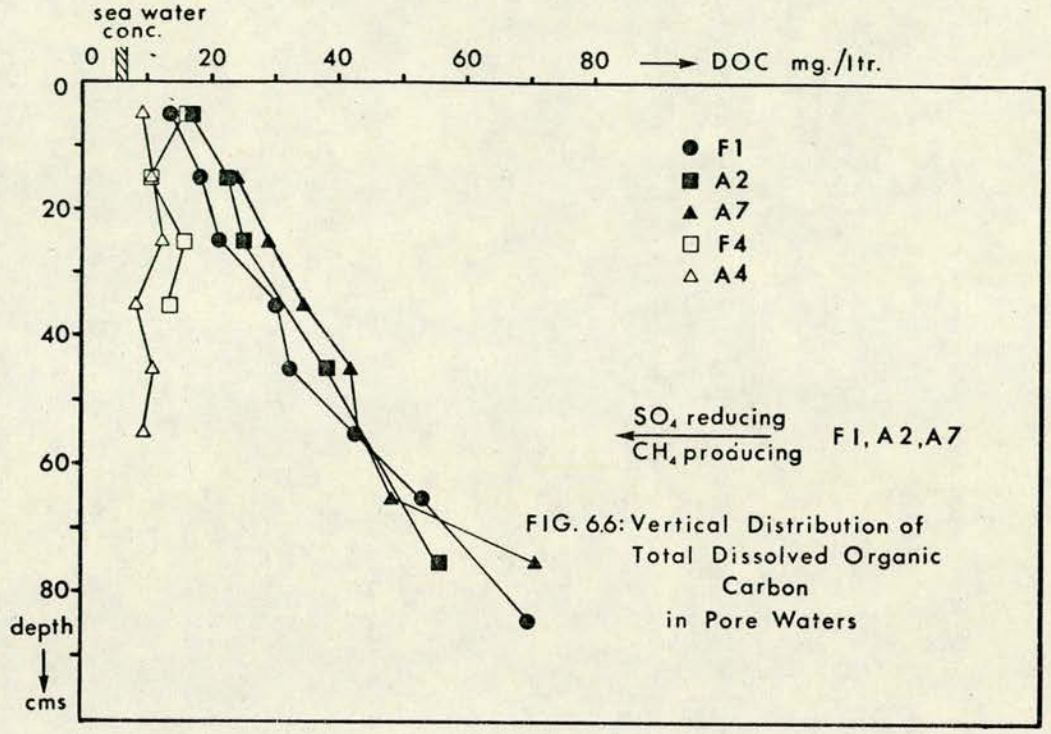


FIG. 6.6: Vertical Distribution of Total Dissolved Organic Carbon in Pore Waters

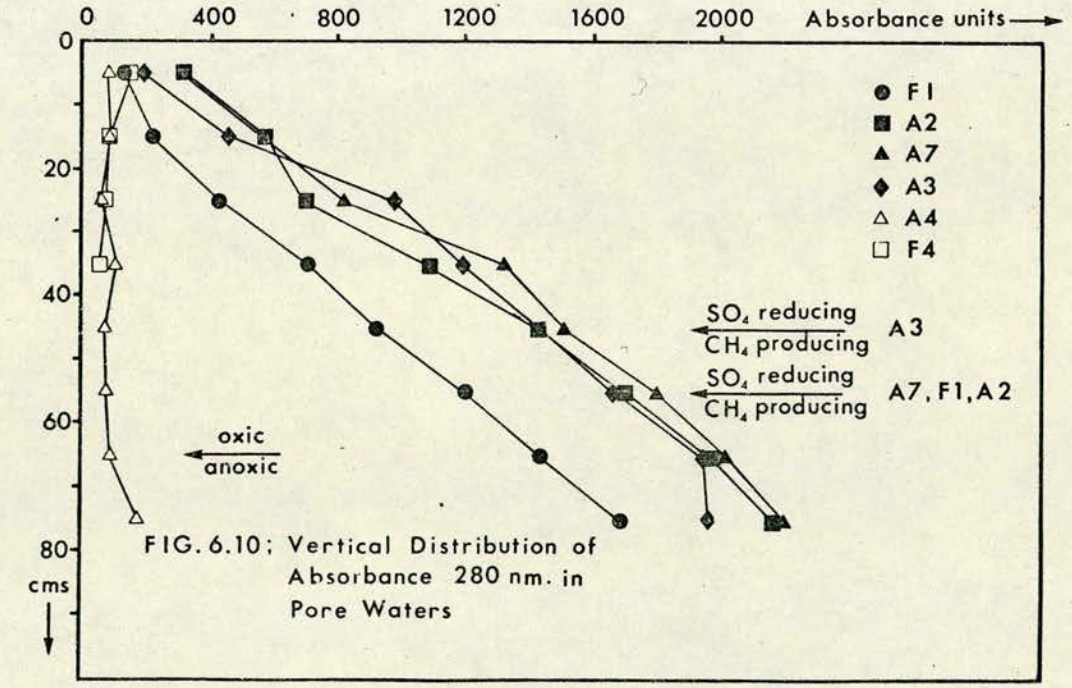


FIG. 6.10; Vertical Distribution of Absorbance 280 nm. in Pore Waters

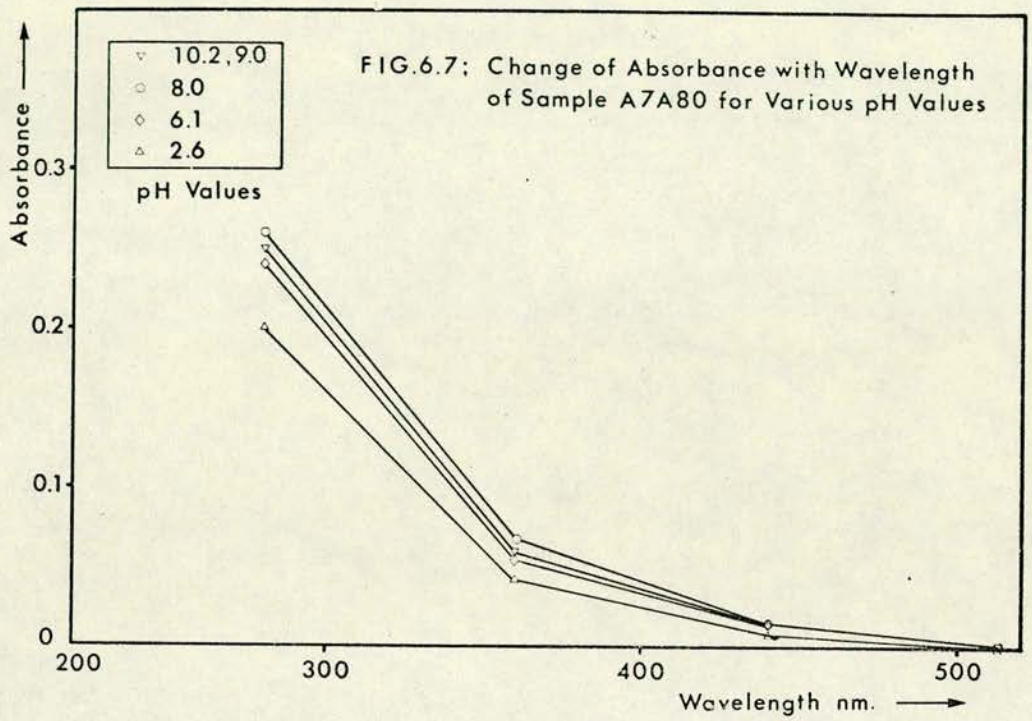


FIG.6.7: Change of Absorbance with Wavelength of Sample A7A80 for Various pH Values

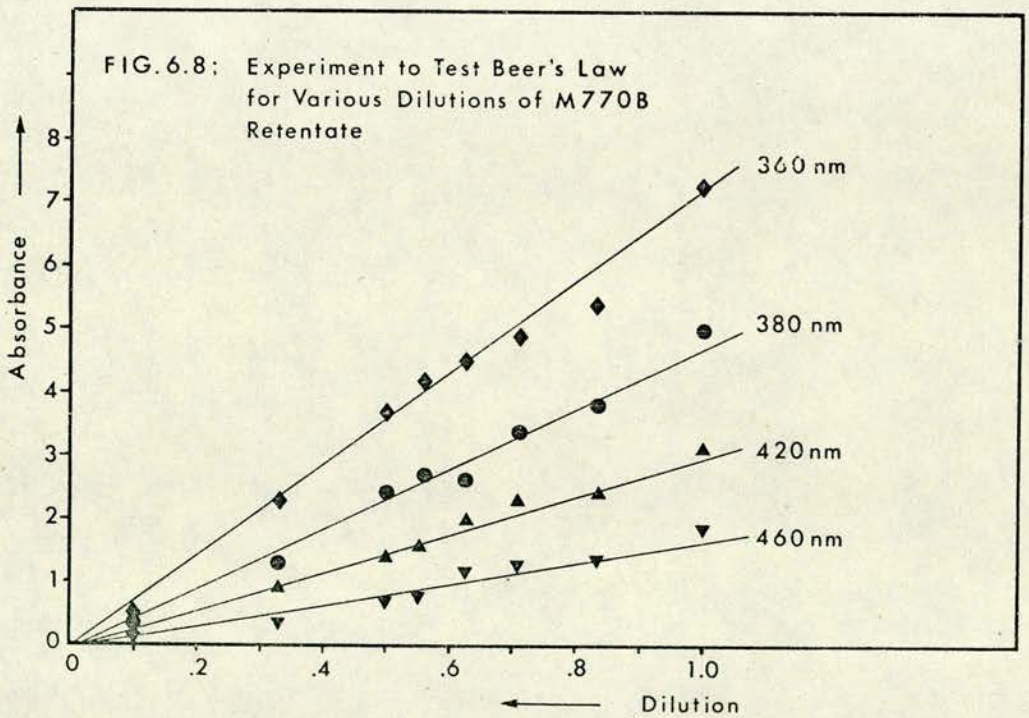


FIG.6.8: Experiment to Test Beer's Law for Various Dilutions of M770B Retentate

vary with pH. The pH of a sample of pore water (A7A80) was adjusted using the minimum volume of concentrated analar NaOH or HCl; pH was measured by a glass combination electrode connected to a pH meter. The results are shown in Figure 6.7. The absorbance remained constant in the range of wavelengths considered ($\pm$5%) for the pH values measured in the pore waters of Loch Duich (7.8 to 8.9).

This range of values for pH is somewhat higher than that quoted by Ben Yaacov (1973) of 6.9 - 8.3. This was probably due to the difference between in situ measurements and those for the pore waters of Loch Duich, which were measured in the laboratory after extraction.

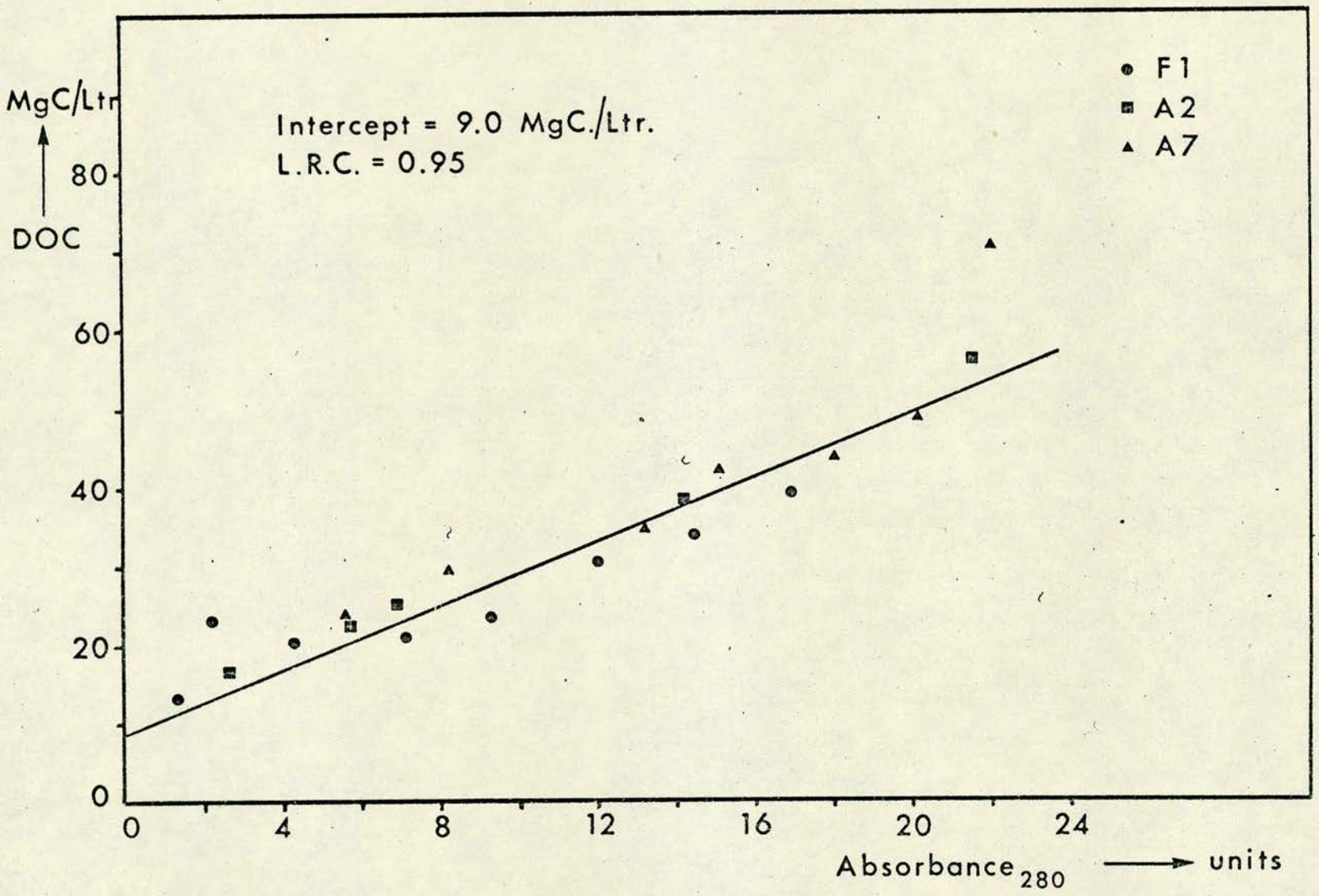
Thus, in using absorbance as a measure of DOC in pore waters it was considered unnecessary to adjust the pH before analysis.

In order to check that Beer-Lambert's law was obeyed, a sample of pore water was diluted by known amounts of freshly distilled and deionised water. The absorbances at a series of wavelengths were then measured relative to a blank of filtered sea water.

Figure 6.8 shows a graph of absorbance at a series of wavelengths against the concentration of the solution which is expressed as the percentage of the undiluted sample. There is a straight line correlation for every wavelength measured within the dilution ranges considered and thus the solutions obeyed the Beer-Lambert law.

Martin and Pierce (1971) used 520 nm as the characteristic wavelength for the measurement of the concentration of "humic" substances in natural waters. No systematic reasoning behind the use of this particular wavelength was given, but 520 nm lies approximately in the middle range of the optical spectrometer used. 465 nm

FIG 6.9; DOC against Absorbance$_{280}$ in Sediment Interstitial Waters



and 430 nm are also used as the characteristic wavelength (Schnitzer and Kahn, 1972), as these produce the largest absorbances using an optical spectrometer. Akiyama (1972) examined the dissolved organic matter (DOM) released by the bacterial degradation of green algae in sea water in different molecular weight fractions. The DOC concentration for each of these fractions was measured by persulphate oxidation (Menzel and Vaccarro, 1964), and compared to the absorbances at 275 nm and 410 nm. The results show that absorbance at 275 nm (Abs_{275}) correlates very well with DOC in all fractions, while Abs_{410} gives an anomalously high absorbance for DOM in the range of M.W. = 1500 - 10,000 (as measured by Sephadex gel).

The absorbance at 280 nm was measured for the pore waters from Loch Duich and compared with the DOC value obtained by a dry combustion method of Gordon and Sutcliffe (1973). The results for Abs_{280} vs. DOC (Figure 6.9) show that there was a good correlation between Abs_{280} and DOC with a linear regression coefficient (L.R.C.) of 0.95 and an intercept of 9.0 mg/litre as measured by a least squares fit. The significance of the intercept is discussed later in this chapter.

Results obtained using Abs_{280} as a measure for DOC

Figure 6.10 shows the change of absorbance with depth for four reducing cores and two oxic cores. The results compare very closely with the DOC on those cores where both DOC and Abs_{280} were measured. In the reducing cores there was an increase of Abs_{280} with depth from 130-308 units at the surface to 1690 - 2200 at 75 cm which was unaffected by the transition from sulphate-reducing to methane-producing conditions. In the oxic cores there was a low and relatively constant value of absorbance (64 - 102 units) which increased significantly

to 172 units below the level in the core at which sulphate reduction commenced. Thus the process by which DOM was produced and accumulated occurred only under anoxic conditions, but was independent of the biogeochemical zones (sulphate-reducing or methane-producing).

In conclusion, light absorbance in the UV range provides a very simple means of quantitatively measuring the concentration of DOC in anoxic pore waters. 280 nm was found to be the most suitable wavelength for this measurement. A series of independent analyses of total DOC was considered to be the best method of calibrating the absorbance data.

6.4 Use of ultrafiltration to partition organics in pore waters into high and low molecular weight fractions

Gjessing (1970) recognised the use of ultrafiltration techniques to divide aquatic humus into a series of molecular weight fractions. Several workers, including Gjessing (1966), Ghassemi and Christman (1968) and Khailov (1963), had previously used Sephadex molecular sieves to separate "humic" materials in natural waters into different size fractions. Gjessing (1973) compared these two methods, showed that there was a poor correspondence due to interaction between the gel used and humus, and concluded that membrane ultrafiltration was preferable for the fractionation of aquatic humus. It was decided in this study to use a UM-2 Diaflo ultrafilter manufactured by Amicon Corporation which has a nominal retention of compounds with a molecular weight $\geqslant 1000$. Ogura (1974) and Wilander (1972) considered the retention of a series of organic compounds of known molecular weight by different grade Diaflo ultrafilters including UM-2. These show an 85% retention for organic matter of

molecular weight = 1000 by the UM-2 filter.

The concentration of DOC was investigated both by UV absorbance (280 nm) and dry combustion for the material retained behind the filter (retentate) and for the material which passed through (ultrafiltrate).

The results for the measurement of absorbance are given in Table 6 III. In order to bring the readings on scale it was necessary to dilute the retentate with distilled water. The value for retentate shown in Table 6 III is corrected for this dilution. All the light-absorbing organic matter was retained behind the ultrafilter, the ultrafiltrate having an absorbance of less than 1% of that of the retentate.

The absorbance of the untreated sample was compared with that predicted, assuming that all the absorbance was in the retentate. The untreated sample has an absorbance greater than the absorbance calculated from the retentate, by a constant factor (240); this difference is noted as being real, but is not explained.

The DOC of the ultrafiltrate and retentate for an oxic core (F4) and an anoxic core (F1) are shown in Figs. 6.11 and 6.12. The concentration of low molecular weight (LMW) organics (MW < 1000) remained approximately constant (10 mg/litre $\pm$ 4 mg/litre) throughout the depth profile for both the oxic and anoxic cores, although there was a small increase with depth of the LMW organics in core F1. The concentration of LMW was approximately twice that of the total DOC (5.1 - 6.7 mg/litre) found in the overlying sea water, demonstrating that there is a diagenetic accumulation of LMW organics in both oxic and anoxic pore waters.

Table 6 III

Calculation of Abs_{280} as a measure of DOC on both sides of the ultrafilter

Sample		Abs_{280} measured(1)	Abs_{280} calc. (2)	(1)-(2)	$\frac{\text{Calc.} + f}{\text{Meas}} \times 100\%$
A2	5	266	183	83	159%
	15	571	323	248	99%
	25	692			
	35	1078	938	140	109%
	45	1420	1180	240	100%
	55	1700			
	65	2070	1824	246	100%

(1) Abs_{280} measured on total untreated sample

(2) Abs_{280} calculated = Abs_{280} retentate x 6 x $\frac{x_r}{x_r + x_u}$

where Abs_{280} is measured on the retentate

$\frac{x_r}{x_r + x_u}$ is the ratio of the weight of retentate to the total weight

and 6 is the dilution factor

f = fudge factor

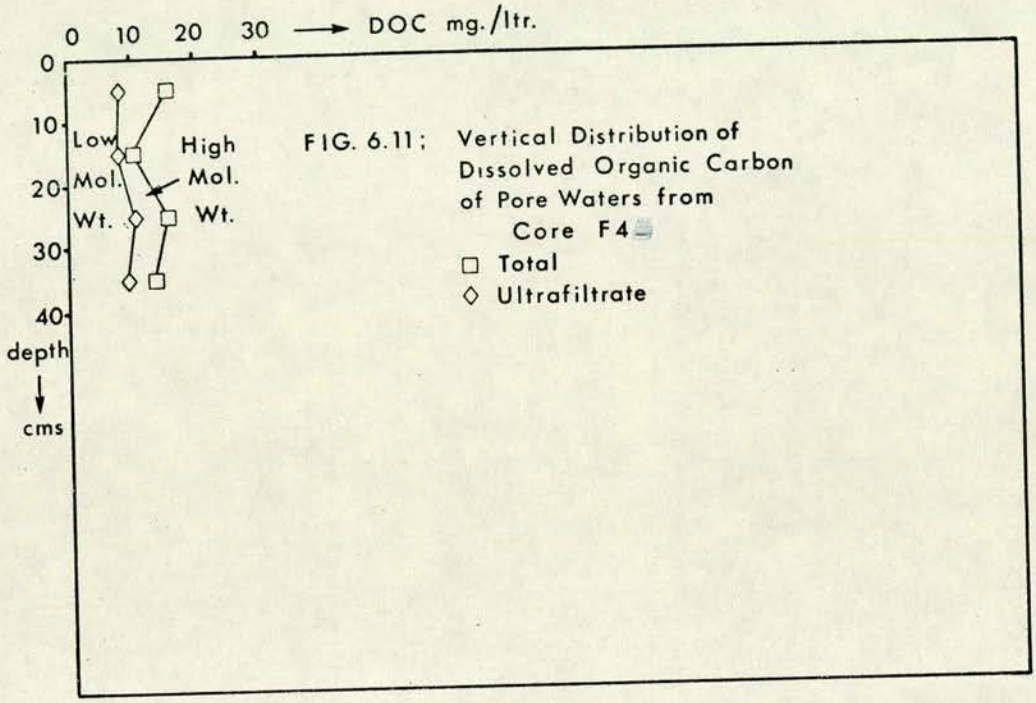


FIG. 6.11; Vertical Distribution of Dissolved Organic Carbon of Pore Waters from Core F4
□ Total
◇ Ultrafiltrate

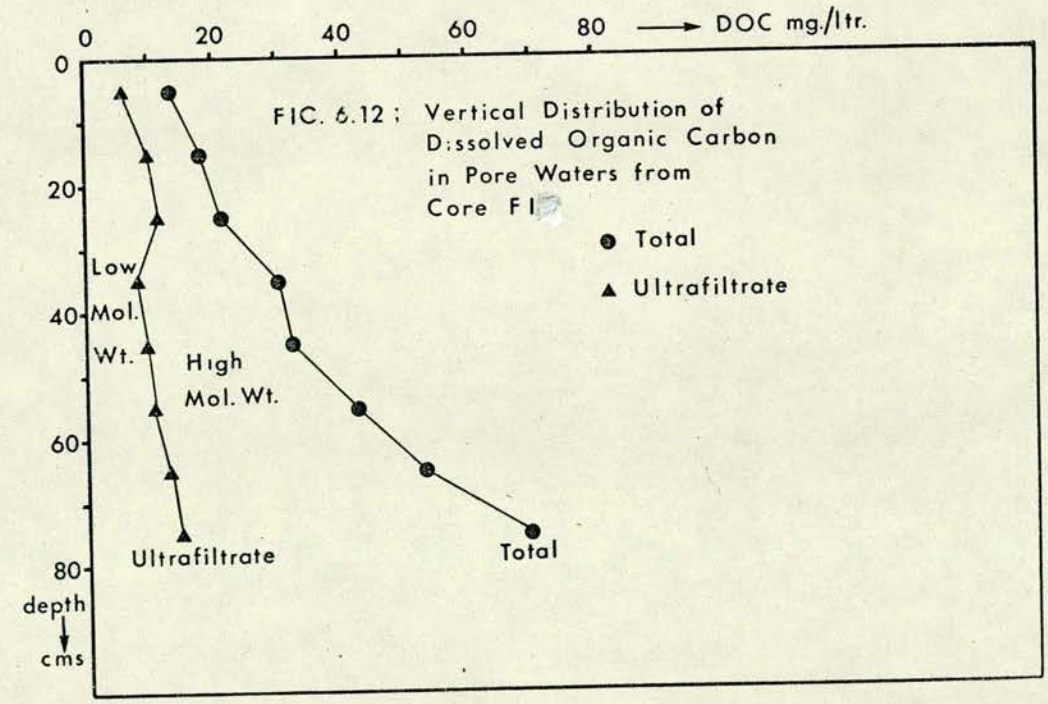


FIG. 6.12; Vertical Distribution of Dissolved Organic Carbon in Pore Waters from Core F1
● Total
▲ Ultrafiltrate

Figure 6.9, the graph of absorbance at 280 nm versus DOC, shows an intercept of 9 mg/litre which corresponds very closely to the LMW fraction, which has no UV absorbance. This demonstrates that absorbance at 280 nm compares very well with the results from dry combustion techniques as a measure of DOC in sediment pore waters from Loch Duich both for the UV absorbing HMW fraction and for the LMW non-absorbing organics.

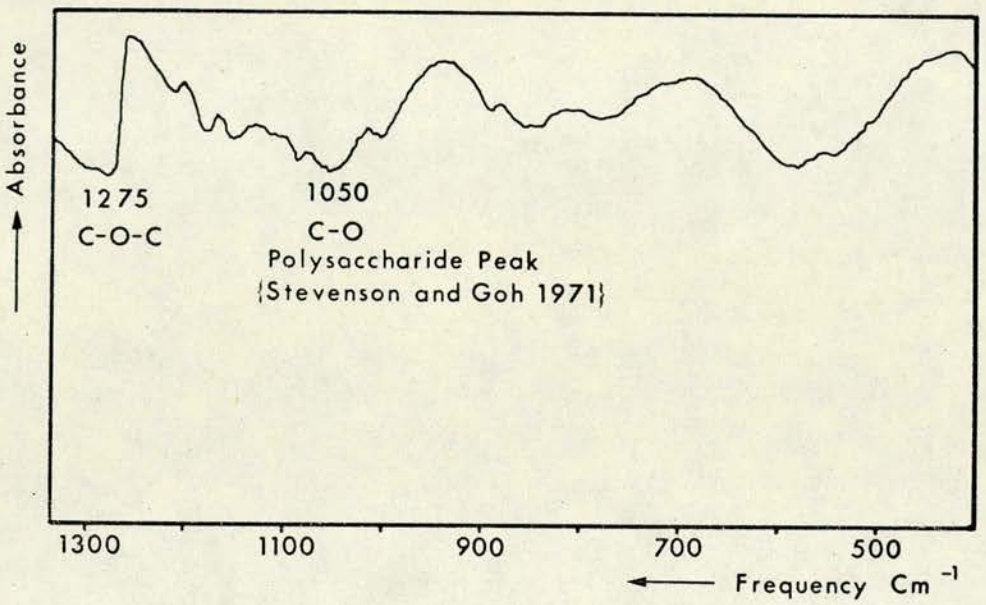
It has been established that there is an accumulation of total DOC in the pore waters of reducing sediments. The analysis of the retentate in core F1 shows that this accumulation is due ~~solely~~ mainly to HMW organics, which increase from 7.6 mg/litre at the surface to 55.2 mg/litre at a depth of 75 cms (Fig. 6.12). HMW organics are also present in core F4 (2.2 - 7.5 mg/litre), but are in lower concentration than those in F1 and do not vary in a systematic way with depth (Fig. 6.11).

Acid insoluble precipitate

When a sample of pore water was acidified to pH = 2, a standard method used in storing waters prior to trace metal analysis (Presley and Kaplan, 1968; Presley et al., 1972), a brown precipitate was formed which was similar in appearance to that formed in the acidified pore waters extracted from Norwegian fjord sediments (J.H. Taylor, pers. comm.). Since humic and hymatomelanic acids can be recognised through their insolubility in mineral acid (Packham, 1964), it was decided to try to characterise this precipitate spectroscopically and chemically to see if it contained significant proportions of these acids. In addition, it was important to ascertain whether the precipitate contained significant quantities of trace metals, since these would affect later analysis of pore water trace metals.

Acidified pore waters were filtered through 0.45 μ Nucleopore^{R} filters and the precipitate retained for characterisation by infra-red spectroscopy (Sholkovitz, 1976) and thin film X-ray emission spectroscopy (Price and Calvert, 1973). The filtrate was adjusted with NaOH to pH 7-9, and the absorbance at 280 nm was measured. This was compared with the Abs_{280} of the untreated sample, and the difference was used as a measure of the DOM removed by acidification and filtration.

The infra-red spectrum of pore water sample A2C40 is shown in Figure 6.13; this spectrum is characteristic of all the precipitates analysed. The principal absorption bands were identified with reference to Stevenson and Goh (1971) and Schnitzer and Kahn (1972). A broad band at 3325 nm which is characteristic of OH bonds is apparent. Since it was not possible with the method of analysis used to completely dry the precipitate, this peak could be due in part to adsorbed water. The peaks at 2900 and 1420 nm are due to C-H bonds, while the complex series of bands between 1520 nm and 1720 nm indicate a series of different C = O bonds (carboxylic, ketones, aldehydes, etc.). The broad peak at 1050 nm was identified by Stevenson and Goh (1971) as C-O bonds in polysaccharides. The spectrum compares very closely with the spectra of humic and fulvic acids from different sources (Stevenson and Goh, 1971), and with that found for the polymeric material separated by dialysis and by acid hydrolysis from the sediment pore waters of Saanich Inlet (Nissenbaum et al., 1971). The spectrum showed qualitatively that the brown material separated by acid precipitation from sediment pore waters was "humic" in nature and was probably humic acid sensu stricto.



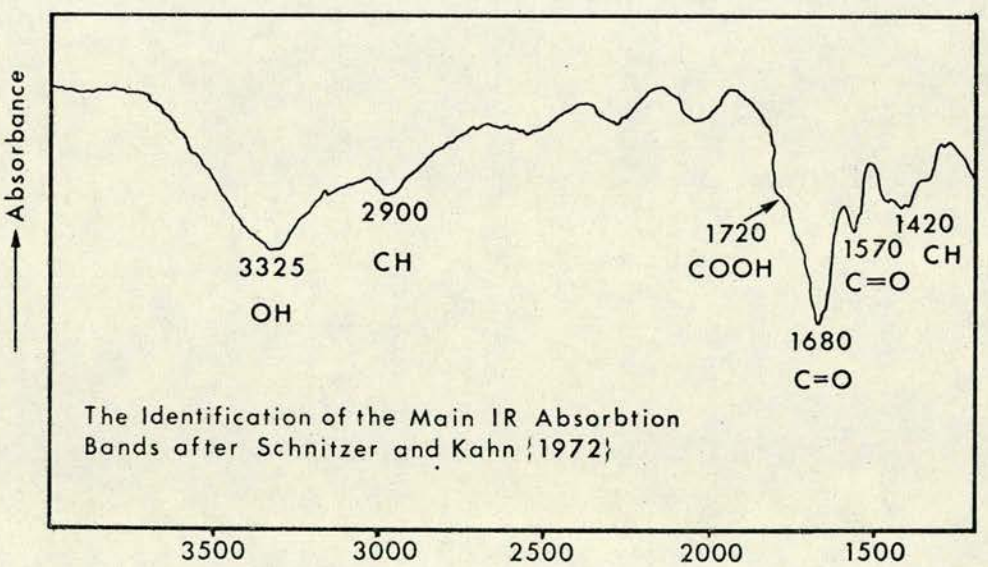


FIG.6.13:IR Absorbtion Spectrum of the Acid Insoluble Humic Acid Precipitate

The measurement of the absorbance (280) of the pore waters before and after acidification and filtration shows no significant decrease (Table 6 IV), and thus it is concluded that the precipitate represents an insignificant fraction of the total DOC present. The increase in absorbance which was found in some samples after acidification and filtration has not been explained.

The precipitate was analysed by X-ray emission spectroscopy for K, Mg, Fe, Ca and P. The results are given in Table 6 V. Because of the errors in the weighing and analysis, the results are only semi-quantitative and the conclusions drawn from them qualitative. Since it was known that the sample contained dry salt, it was necessary to correct the analyses of Ca and Mg for this salt. It was assumed that all the K present in the sample was sea salt, since monovalent ions tend not to form chelates in the presence of divalent ions (Stumm and Morgan, 1970). Assuming a K/Mg = 0.299 and K/Ca = 0.937 in sea salt (Culkin, 1965), the excess Ca and Mg was calculated and assumed to be bound to the "humic" material. The results show that the acid precipitate contains no significant quantities of complexed Ca or Mg. This result contrasts with that of Nissenbaum et al. (1971) for the "humic" material separated from the pore waters of Saanich Inlet by dialysis, which contained significant quantities ($\sim$2%) of Ca. The difference in these results may be due to the contrasting methods of extraction, the hydrogen ions tending to displace all the calcium ions from the acid-precipitated "humic" material. The acid precipitate contained significant quantities of iron (0.1 - 0.9%), as did the polymeric material of Saanich Inlet (0.3%) (Nissenbaum et al., 1971). Thus the iron may be bound more strongly

Table 6 IV

Absorbance (280 n m.) of untreated pore waters from core A2 compared to the absorbance measured after the removal by filtration of the acid insoluble precipitate (measured at pH = 8)

Depth (cms)	Untreated Absorbance	Absorbance after Filtration
5	266	181
15	571	467
25	692	645
35	1078	1330
45	1420	1890
55	1700	1940
65	2070	2040
75	2160	-

Table 6 V

Concentration of K, Ca, Mg, Fe and P in the acid insoluble humic acid precipitate derived from the anoxic pore waters of core A2 measured by thin film X-ray emission spectroscopy (All weights are given in micrograms)

Depth (cms)	Wt of Precipitate	Wt of K (2)	Wt of Salt (1)	Wt of Humic Acid
5	1510	3.9	364	1146
15	930	7.0	654	276
25	1130	8.7	813	317
35	820	3.3	308	512
45	2150	4.7	439	1711
55	1090	7.9	738	354
65	450	2.7	252	198
75	1390	4.3	402	988

(1) Calculated from the analysis of K assuming that all the K is in the dried pore water and that pore water salt has major elements present in the same ratio as is found in sea water.

(2) Measured weight of element in acid insoluble precipitate.

(3) Measured element - weight of element calculated to be present in salt.

Depth (cms)	Wt of Ca (2)	Wt of Ca in salt (1)	Excess Ca (3)	Wt of Mg (2)	Wt of Mg in salt (1)	Excess Mg (3)
5	3.6	4.1	-	13.0	13.8	-
15	6.6	7.4	-	17.5	24.9	-
25	7.1	9.2	-	20.8	30.9	-
35	3.6	3.5	0.1	12.1	11.7	0.4
45	6.8	4.9	1.9	15.7	16.7	-
55	6.8	8.3	-	30.3	28.0	1.7
65	5.0	2.8	2.2	10.3	9.6	0.7
75	5.4	4.5	0.9	8.7	16.0	-

There is no significant excess of Ca or Mg.

Depth (cms)	Wt of P (2)	P/Humic acid (x100%)	C/P Ratio (4)	Wt of Fe (2)	Fe/Humic acid (x100%)
5	10.9	0.1%	53	0.8	0.07%
15	22.9	8.3%	6	1.1	0.4%
25	24.6	7.8%	6	1.3	0.41%
35	16.9	3.3%	15	1.0	0.2%
45	29.9	1.7%	29	0.9	0.05%
55	14.6	4.1%	12	1.1	0.3%
65	6.9	3.5%	14	1.7	0.9%
75	18.7	1.9%	26	1.1	0.1%
Average		3.8%	20		0.3%

(4) Wt of Carbon is calculated by assuming that 50% of the Humic acid fraction of the acid insoluble precipitate is Carbon.

and possibly in a different manner from the calcium, since a significant fraction of it resisted displacement by hydrogen ions. The acid precipitate also contained (0.1 - 8.3%) phosphorus within it which, assuming the carbon represents 50% of the "humic" material (Black and Christman, 1963; Manskaya and Drozdova, 1968), results in a C/P ratio of 53 to 6; this compares with the C/P ratio of (40 - 50) for "humic" flocculants separated from river water by acid and sea water flocculation (Sholkovitz, 1976).

It was concluded from these results that the precipitate flocculated out of pore waters on the addition of acid is "humic" (probably humic acid sensu stricto) and is similar in chemical and spectroscopic properties to the polymeric material separated from the pore waters of Saanich Inlet by dialysis (Nissenbaum et al., 1972); it represents only a small fraction of the total coloured material and DOC (approx. 1%) present in the pore waters.

6.5 Discussion of results and conclusions

Composition of dissolved organic matter

The value for dissolved organic carbon is used here as a measure of the total concentration of organic matter present. Previous studies on the carbon content of "humic" fractions isolated from soil, sediment and water have shown that humic acids have carbon content estimated as 53.7 - 60.4% (Schnitzer and Kahn, 1972) and 52 - 62% (Manskaya and Drozdova, 1968) and fulvic acids 42.5 - 50.9% (Schnitzer and Kahn, 1972), 44 - 48% (Manskaya and Drozdova, 1968) and 40.6% (Black and Christman, 1963). The carbon content of the HMW dissolved organic matter separated from the pore waters of

Saanich Inlet was estimated as 30 - 40% (Presley et al., 1972). Thus the DOC represents 30 - 50% of the DOM in the pore waters of Loch Duich. Phosphorus represented 1 - 5% of the humic acid fraction in the pore waters, a result which is similar to the P content found in the humic acid separated from river water by Sholkovitz (1976).

No attempt was made in this study to analyse pore waters for common organic molecules; previous work has demonstrated the presence of amino acids and carbohydrates in both sediments (Degens and Mopper, 1973) and the exudate from algae (Otsuki and Hanya, 1972), while Johns and Onder (1975) and Brown et al. (1972) have shown the presence of carboxylic acids; the latter have also demonstrated the presence of free hydrocarbons. It seems likely that if sediments and their pore waters are analysed for any of the major organic components of living cells, these will be found to be present (Siegel, 1972).

A number of degradation studies have been made on "humic" material separated from marine sediments and natural waters; the products analysed including the following: carbohydrates and amino acids (Nissenbaum et al., 1972), phenols and enols (Shapiro, 1957), quinones (Rashid, 1972) and a series of oxygen-containing functional groups (carbonyls, carboxyls and hydroxyls) (Rashid and King, 1970). Christman and Ghassemi (1966) suggest the "humic" molecule in natural waters to be a multibasic, multicarboxylic aromatic-aliphatic molecule containing no nitrogen, while other workers have shown this "humic" material to be a highly complex polycondensate containing at least significant proportions of carbon, nitrogen, hydrogen and oxygen

(Schnitzer and Kahn, 1972; Rashid and King, 1970; Nissenbaum et al., 1972).

The LMW fraction (<1000) was colourless both to visible and UV light and was presumed to contain a high proportion of the small organic molecules listed above. There was no evidence for fulvic acid being present; the 34% fulvic acid with MW ≤ 700 in coastal marine sediments (Rashid and King, 1969) does not have an immediate counterpart of dissolved fulvic acids with a MW <1000 in the interstitial waters of coastal marine sediments. The HMW fraction contains all the colour, and if there is a colourless component within this fraction, it was not possible to detect it by the methods of analysis used. This HMW fraction has the spectrographic properties of "humic" material, while the infra-red spectrum of the acid insoluble precipitate was similar to that found for humic acid (Ziechmann, 1964; Schnitzer, 1965; Swift et al., 1970; Stevenson and Goh, 1971, and Nissenbaum et al., 1971). Three fractions as defined by chemical and spectrographic criteria were recognised in the HMW organics of the anoxic pore waters.

1) A humic acid fraction which was characteristically insoluble in acid solution (pH = 2) and provided an infra-red spectrum very similar to that found by Nissenbaum and Kaplan (1971) for the colloidal fraction dialysed from the pore waters of Saanich Inlet. This fraction represents a very small proportion (approx. 1%) of the total DOM present.

2) The major fraction on the basis of spectral ratio is fulvic acid with

3) an unknown quantity of the exudate of decomposing algae (Sieburth

and Jensen, 1968a,b; Otsuki and Hanya, 1972a,b) which is thought by Kalle (1966) and Nissenbaum et al. (1971) to contain a high proportion of melanoidins; this fraction is identified as having a higher E_4/E_6 spectral ratio than either humic or fulvic acids.

Diagenetic trends observed with depth

Figure 6.14 represents the changes in DOC related to the biogeochemical zones found in the sediment pore waters. For the purpose of this diagram, the results of the analyses from sea water, an oxic core (F4) and an anoxic core (F1) are superimposed in the sequence defined in Chapter 5.

The DOC found in oxic pore waters is significantly greater than that found in the overlying sea water, showing that there is a diagenetic reaction occurring which results in the formation of DOM in pore waters throughout the sediment column. Below the oxic/anoxic redox boundary there is an increasing accumulation of DOM which is unaffected by the boundary between sulphate reduction and methane production. This accumulation is present entirely in the HMW fraction, the LMW fraction remaining virtually constant throughout the sediment column. Nissenbaum et al. (1971), using a limited number of data points, also found that there was an increasing accumulation of HMW polymeric material with depth in the pore waters of Saanich Inlet.

These observations together with the increase in the spectral ratio with depth show clearly that there is an autochthonous production and accumulation of HMW (>1000) yellow-coloured "humic" material. This material is mainly fulvic acids, but also contains another fraction which may be similar in chemical composition to

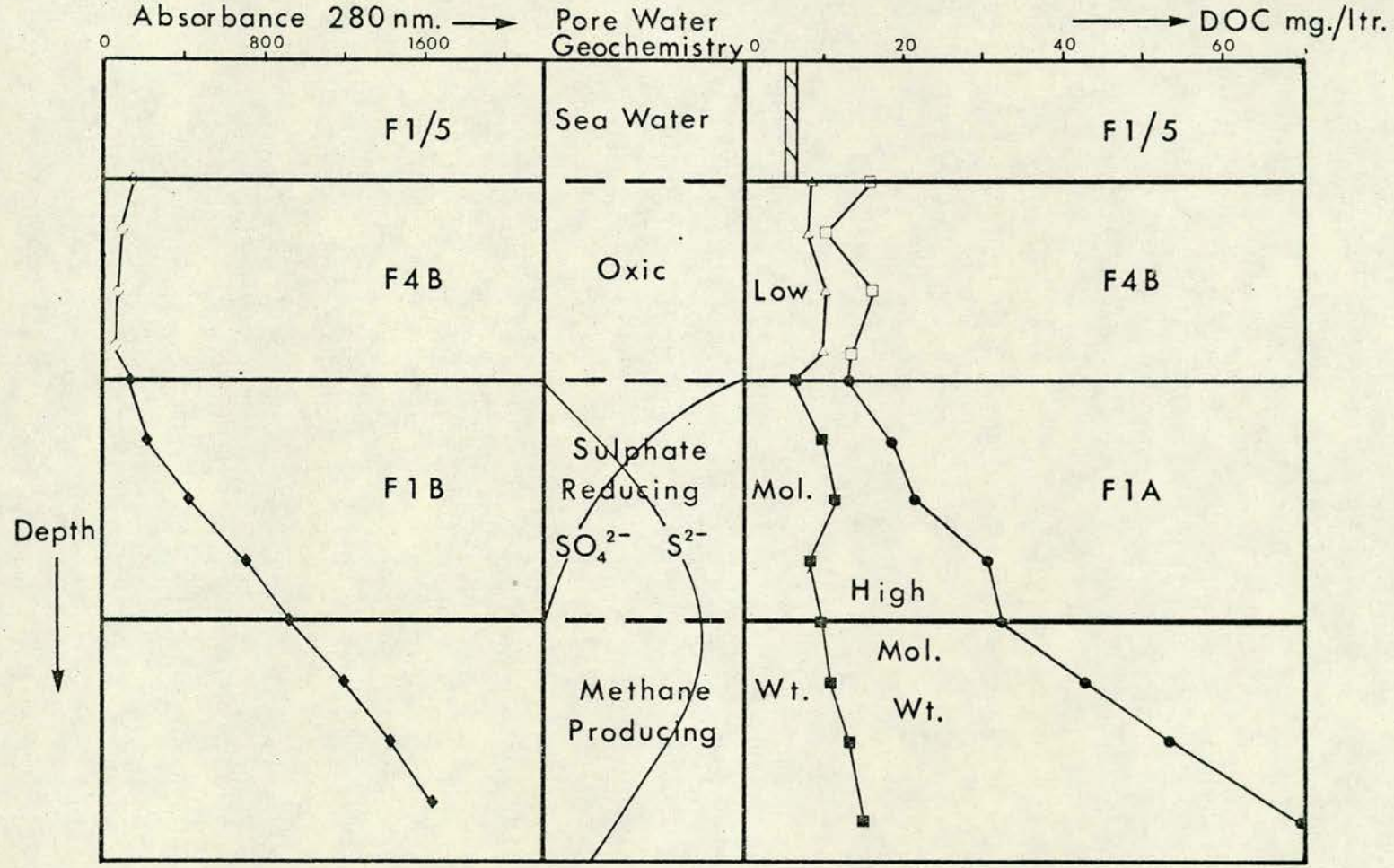


FIG.6.14:Diagrammatic Representation of Changes in DOC in Successive Biogeochemical Zones

a melanoidin. This latter fraction is present in increasing proportions with depth.

Processes involved in the production and removal of DOM in sediment interstitial waters

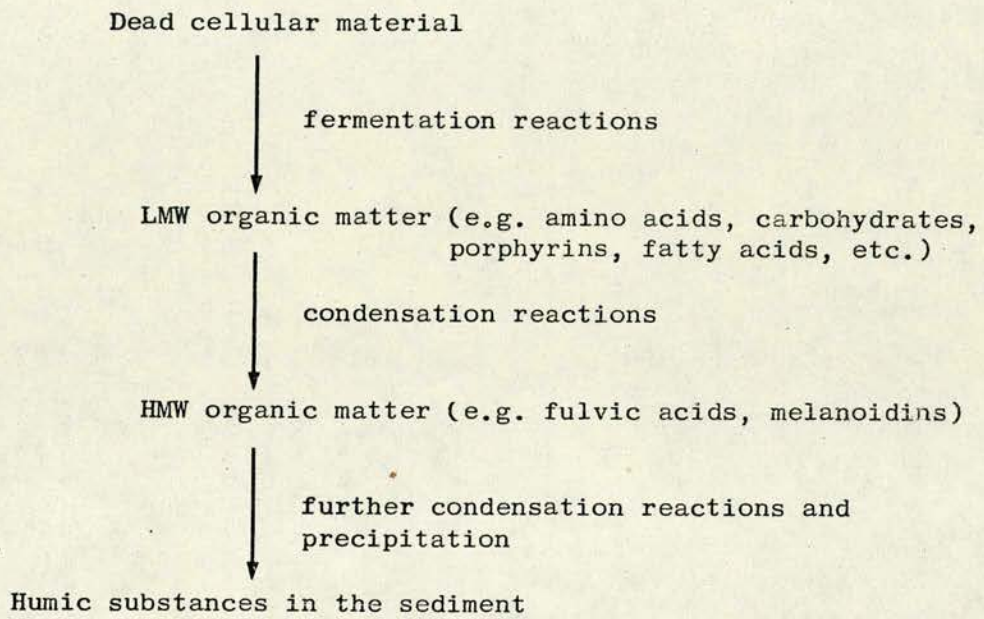


Figure 6.15 A schematic diagram to show possible steps in the conversion of dead cellular material to solid humic substances in the sediment (after Nissenbaum et al., 1971)

The accumulation of "humic" substances in anoxic pore waters is independent of the type of metabolic oxidation taking place and confirms the presence of a third metabolic process which is independent of sulphate reduction and methane production. Such a fermentation process was postulated by Claypool and Kaplan (1974) to provide the low molecular weight fatty acids required by sulphate reducing bacteria for their metabolism (Postgate, 1965) and shown to be thermo-

dynamically feasible. They showed two possible types of fermentation reactions which could be occurring in sedimentary pore waters.

$$\text{Glucose} \longrightarrow \text{lactate} + \text{ethanol} + CO_2$$

$$\text{Alanine} + 2\ \text{glycine} + 2H_2O \longrightarrow 3\ \text{acetate} + CO_2 + 3NH_3$$

It is known from the results given above that such LMW organics are present in a constant concentration in the pore waters. They do not accumulate in sediment pore waters, but tend to condense to form HMW organic matter. One of the possible condensation reactions which may be occurring is the Maillard or Browning reaction, which converts amino acids and carbohydrates into melanoidins (Manskaya and Drozdova, 1968). Such a condensation reaction would explain the observed value and changes with depth of the spectral ratio in the pore waters of Loch Duich as well as the known presence of a large proportion of amino acids and carbohydrates in the hydrolytic breakdown products of the polymeric humic material separated from the pore waters of Saanich Inlet (Nissenbaum et al., 1971).

This breakdown and condensation process was examined in the laboratory by Sieburth and Jensen (1968a, 1968b) and by Otsuki and Hanya (1972a, 1972b). Algal material was allowed to decompose in controlled laboratory conditions and the DOM produced analysed chemically and spectroscopically. Sieburth and Jensen (1968a) showed that this DOM had many of the properties of "humic" substances, Gelbstoff. Otsuki and Hanya (1972a, 1972b) showed that this yellow high molecular weight "humic" material was produced by the microbial breakdown of algal material under both aerobic and anaerobic conditions, but that the rate of production and the proportion of DOM to

mineralised product was much greater under anaerobic conditions. These laboratory experiments show that the bacterial decomposition of algal material is a likely mechanism to produce the observed nature and distribution of DOM in the pore waters.

Kemp and Mudrochova (1973) and Kemp and Wong (1974) examined humic substances in the surface sediments from Lakes Ontario and Erie. They concluded that a large proportion of these humics was formed by in situ diagenetic reactions in which combined amino acids in the interstitial waters are intermediates between the primary aquatic detritus and sedimentary humic acids. Nissenbaum and Kaplan (1972) examined the chemical and isotopic properties of marine humic substances and concluded that most of the humic acids are also derived in situ from the microbial decomposition of cellular material. They suggest a pathway of (1) degraded cellular material → (2) water soluble complex containing amino acids and carbohydrates → (3) fulvic acids → (4) humic acids → (5) kerogen. The evidence presented in this chapter is entirely consistent with such a model for the breakdown, alteration and deposition of marine organic matter.

CHAPTER 7

TOTAL ORGANIC MATTER IN SEDIMENT

7.1 Introduction

The elements C, N, P and I in the sediment were measured in order to compare the organic matter in Loch Duich to that in other shallow marine coastal environments. Total organic carbon (TOC) was used as a measure of the quantity of organic matter present, while elemental ratios (C/N, C/P and I/C) were used to investigate the nature of the organic matter and diagenetic changes within the sediment.

Three chemical treatments (see Appendix B) were performed to separate the trace metals in the sediment into different phases, the fractions bound in organics, oxides and humics. The C, N and I were measured to examine the effectiveness and specificity of each of these treatments. Data obtained on the organic matter in the sediment was used to relate the accumulation of nutrients and DOM in the pore waters to the decomposition of organic matter within the sediment.

7.2 Geochemistry of organic matter in sediments

Analytical procedures

Subsamples of dry ground sediment were analysed for a series of the principal elements associated with organic matter in the sediment. (See Appendix B for details of the methods used.) Total carbon was measured by two dry combustion methods. The samples collected in

April 1974 were analysed using a LECO induction furnace with a manometer attached to measure the carbon dioxide evolved volumetrically, while the samples collected in February 1975 were analysed using a Perkin-Elmer 240 elemental analyser. The results obtained by these two methods were compared by running duplicates and found to be equal ($\pm$5%). The total organic carbon (TOC) was obtained by subtracting the carbonate carbon, measured by acidifying the sample and measuring the carbon dioxide released volumetrically, from the total carbon. Total nitrogen was measured by two methods, the micro-Kjeldahl method of McKenzie and Wallace (1954) as adapted by Doff (1970) and dry combustion in the Perkin-Elmer 240 elemental analyser. As with the total carbon duplicate samples were run and found to be comparable ($\pm$5%). Total phosphorus was analysed by an X-ray fluorescence method similar to that described by Rose et al. (1963), as used by Taylor (1974). Total iodine was measured on sediment samples using the X-ray emission method of Price et al. (1970). Silver iodide in an iodine free sediment matrix was used as the standard.

The analyses presented in Table 7 I are corrected for the diluting effect of the salt content of the sediment. The proportion of bicarbonate, ammonia and phosphate present in this salt is insignificant as compared to the total quantities of C, N and P in the sediment. The iodine content of the interstitial waters was not measured, and thus a salt correction for this value could not be applied. It is known that the pore waters of recent sediments are considerably enriched compared to the overlying sea water. Bojanawski and Paslawska (1970) found a dissolved iodine content of up to 1.9 ppm in the sediment pore waters from the southern Baltic Sea,

which compares to the typical sea water value of 60 ppb (Goldberg, 1965). This concentration, if present in the pore waters of Loch Duich, is not significant in relation to the 100 - 500 ppm total iodine found in the sediment. Shishkina and Pavlova (1965) analysed a series of sediments for both sedimentary and pore water iodine. The proportion of iodine in the pore waters was less than 10% of the total except for three samples of Black Sea sediments collected at depths greater than 4 metres. A salt correction for the iodine content within the pore waters in this study is thus not necessary.

7.3 Results: total organic carbon (TOC)

The concentrationsof total organic carbon within different sediment cores in Loch Duich are given in Table 7 I. Using a conversion factor of 1.94 (Bader, 1954), the overall range of 3.73% to 8.40% (av. = 5.6%) TOC represents 7.24% to 16.30% total organic matter. The majority of the samples are within the range 5 - 7% organic carbon (i.e. 10 - 14% TOM).

This value of TOC is typical of the sediments in fjords; for comparison, Saanich Inlet, British Columbia is 0.95 - 5.05% (Brown et al., 1972), Oslofjord, Norway is 0.87 - 7.21% (Doff, 1970) and Loch Sunart, Scotland is 1.34 - 11.33% (S. Stanley, unpublished data). It is somewhat higher than the usual TOC for "normal" coastal marine sediments 2.3 - 5.0% (Rashid and King, 1970) and the sediments of the Santa Barbara basin, 2.1 - 3.1% (Prashnowsky et al., 1961) and significantly greater than deep sea sediments such as the Argentine basin 0.41 - 1.72% (Stevenson and Cheng, 1972).

Figure 7.1 shows the changes in TOC with depth for 6 cores; A2, F1, A3 and A7 are reducing cores from the central basin, while

Table 7 I

Concentration of elements associated with organic matter in the sediments of Loch Duich

Core and depth (cms)		C (%)	N (%)	P (%)	I (ppm)	C/N	I/C_4 ($\times 10^4$)
A4	0	6.26	0.41		136	14.6	21.7
	10	4.78	0.28		80	16.8	16.8
	20	4.62	0.23		88	19.0	19.1
	30	6.00	0.36		80	16.4	13.4
	40	7.11	0.36		67	18.2	9.5
	50	8.33	0.45		89	17.8	10.7
	60	8.40	0.36		73	22.2	8.7
	70	7.48	0.43		53	16.7	7.1
F4	0	6.24	0.44	0.17	232	14.2	37.1
	5	5.95	0.41	0.12	176	14.6	29.7
	10	5.90	0.38	0.13	178	15.4	30.2
	15	5.13	0.35	0.12	148	14.8	28.8
	20	4.64	0.29	0.12	105	15.8	22.6
	25	4.08	0.27	0.12	94	15.4	23.0
	30	5.18	0.32	0.13	104	16.4	20.1
	35	5.58	0.36	0.13	94	15.6	16.8
	40	6.38	0.39	0.16	82	16.4	12.9
A7	0	5.52	0.48		314	10.9	57.0
	10	5.25	0.43		322	11.7	61.4
	20	5.63	0.45		268	11.9	47.6
	30	5.73	0.44		196	12.4	34.3
	40	6.20	0.45		233	13.0	37.6
	50	6.54	0.42		214	14.9	32.8
	60	6.85	0.48		182	13.6	26.5
	70	6.51	0.48		207	13.1	31.8
A3	0	6.71	0.46		354	13.9	52.8
	10		0.41				
	20	7.50	0.49		215	14.6	28.7
	30	6.55	0.49		185	13.6	28.2
	40	6.67	0.45		193	14.1	28.9
	50	7.14	0.45		182	15.1	25.4
	60	5.86	0.40		179	13.9	30.6
F1	0	5.85	0.50	0.14	498	11.6	85.1
	5	3.73	0.33	0.13	417	11.4	111.8
	10	5.52	0.51	0.12	399	10.9	72.4
	15	5.28	0.49	0.10	395	10.7	74.9
	20	5.21	0.46	0.09	356	11.4	68.3
	25	5.13	0.47	0.09	323	10.9	63.1
	30	5.49	0.44	0.09	285	12.4	51.9
	35	5.09	0.45	0.09	294	11.3	57.7
	40	5.26	0.42	0.09	268	12.6	50.9

continued

Table 7 I (continued)

Core and depth (cms)		C (%)	N (%)	P (%)	I (ppm)	C/N	I/C $(x10^4)$
F1	45	5.01	0.42	0.09	254	11.9	50.8
	50	5.16	0.44	0.09	265	11.7	51.4
	55	4.91	0.42	0.09	249	11.7	50.7
	60	4.76	0.40	0.09	238	12.1	50.0
	65	4.88	0.42	0.09	229	11.6	46.8
	70	5.06	0.39	0.09	217	12.9	42.9
	75	6.22	0.48	0.09	213	13.1	34.3
	80	7.48	0.54	0.11	237	13.9	31.7
A2	0	5.10	0.44	0.11	322	11.6	63.2
	10	4.72	0.44	0.08	290	10.7	61.5
	20	5.25	0.43	0.10	259	12.2	49.4
	30	5.44	0.41	0.10	198	13.3	36.4
	40	6.67	0.47	0.10	237	14.1	35.5
	50	6.68	0.50	0.09	259	13.3	38.7
	60	5.91	0.46	0.09	215	12.8	36.5
	70	5.68	0.47	0.10	191	12.0	33.6
	80	6.43	0.49	0.11	203	13.0	31.6

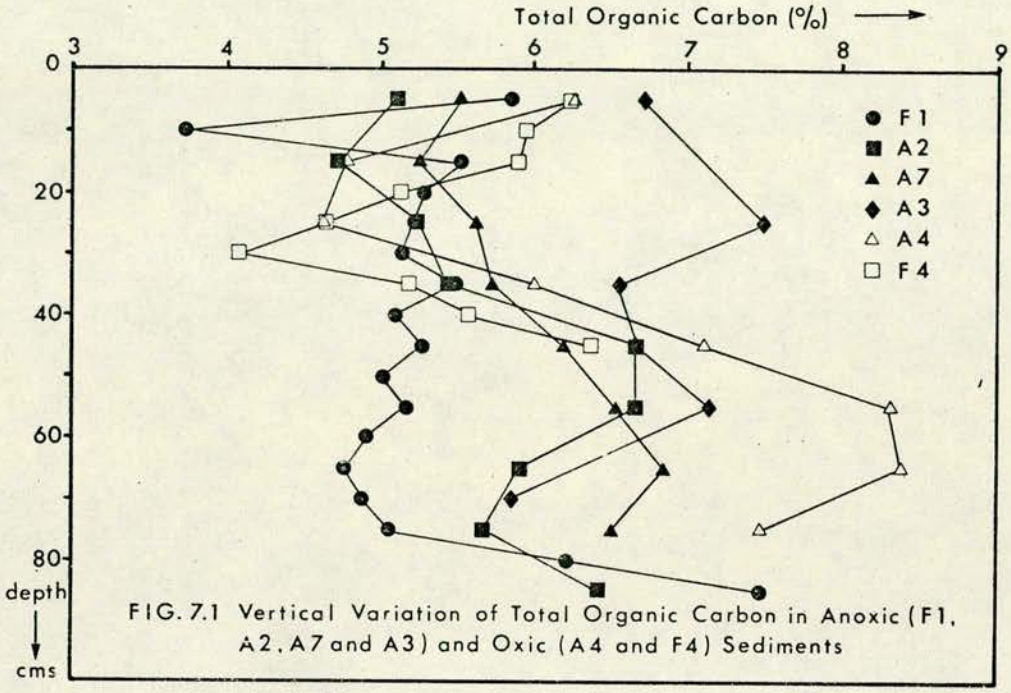


FIG. 7.1 Vertical Variation of Total Organic Carbon in Anoxic (F1, A2, A7 and A3) and Oxic (A4 and F4) Sediments

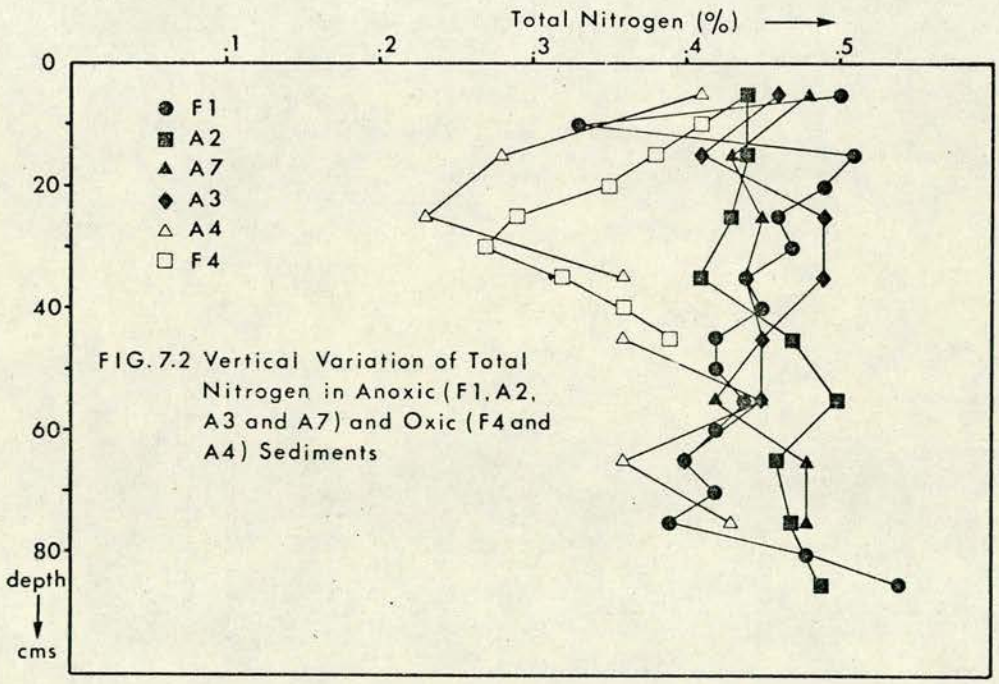


FIG. 7.2 Vertical Variation of Total Nitrogen in Anoxic (F1, A2, A3 and A7) and Oxic (F4 and A4) Sediments

A4 and F4 are oxidising cores from Loch Beg. The TOC concentration for the oxidising cores and the reducing cores are similar in value, and in both there are no observable trends with depth; a similar result to that found in Saanich Inlet (Brown et al., 1972), Oslofjord (Doff, 1970) and off the California coast (Rittenberg et al., 1963). Kaplan et al. (1963) show that there is a decreasing concentration of total organic carbon with depth in sediments from the Santa Barbara basin. Sholkovitz (1973) also analysed the TOC of a core from the Santa Barbara basin and shows that although there is some decrease in total organic carbon there is a considerable scatter in the results. Table 7 I shows the value for total nitrogen and total phosphorus within the sediment. It is known that both these elements are partitioned between an inorganic phase and an organic phase. Stevenson and Cheng (1972) found that it is necessary to correct the total nitrogen concentration for the quantity of fixed NH_4^+ present in the lattice of aluminosilicates which represented 10 - 25% of the total nitrogen in the sediment of the Argentine basin. This correction is insignificant in the sediments of Loch Duich because of the larger proportion of organic matter present (approximately 5 times).

The overall concentration of total nitrogen in the sediments of Loch Duich is 0.27 - 0.54% with somewhat lower results being obtained in the sediments of Loch Beg (average 0.405%) as compared to those in the central basin (average 0.45%). These concentrations are similar to those found in the Santa Barbara basin, 0.28 - 0.38% (Prashnowsky et al., 1961) while being significantly greater than those found in the Argentine basin $\sim$0.075% (Stevenson and Cheng, 1972). No discernible trends with depth within each core can be observed (Fig. 7.2).

The concentration of total phosphorus in the basin sediments of Loch Duich are in the range 0.09 - 0.14% (av. 0.10%), which is lower than the average concentration in the sediments of Loch Beg 0.12 - 0.17% (av. 0.13%). Sholkovitz (1973) analysed the total phosphorus content for the sediments of the Santa Barbara basin and found values 0.13 - 0.15% very similar to those in this study. However, he also measured the sediment for organic phosphorus, which was 0.015 - 0.036%. This demonstrates that the use of total phosphorus as a measure of the phosphorus bound in organic matter is not possible without prior chemical treatment to separate these two phases. No such separation was done on the sediments of Loch Duich, and thus no information is available on the relative importance of organic and inorganic phosphorus in the sediments of Loch Duich.

The surface concentration of total iodine in the basin cores, 314 - 498 ppm, was similar to typical oceanic and coastal marine sediments, approx. 500 ppm (Shishkina and Pavlova, 1965), the surface sediments off S.W. Africa, 100 - 900 ppm (Price and Calvert, 1973a), the Barents Sea, 60 - 828 ppm (Price et al., 1970) and in Loch Etive, 468 ppm (Doff, 1970). The concentration of iodine in the surface sediments of Loch Beg, 132 - 232 ppm are significantly lower than those found in the central basin of Loch Duich; the difference is not due to the concentration of organic matter present, since the TOC in both localities is the same (5.5% vs 5.8%).

Figure 7.3 represents the change of total iodine with depth for 6 cores. These show that for every core there is a decrease in concentration of total iodine with depth. The profiles for both core F1 and F4 show a simple exponential decrease in concentration of

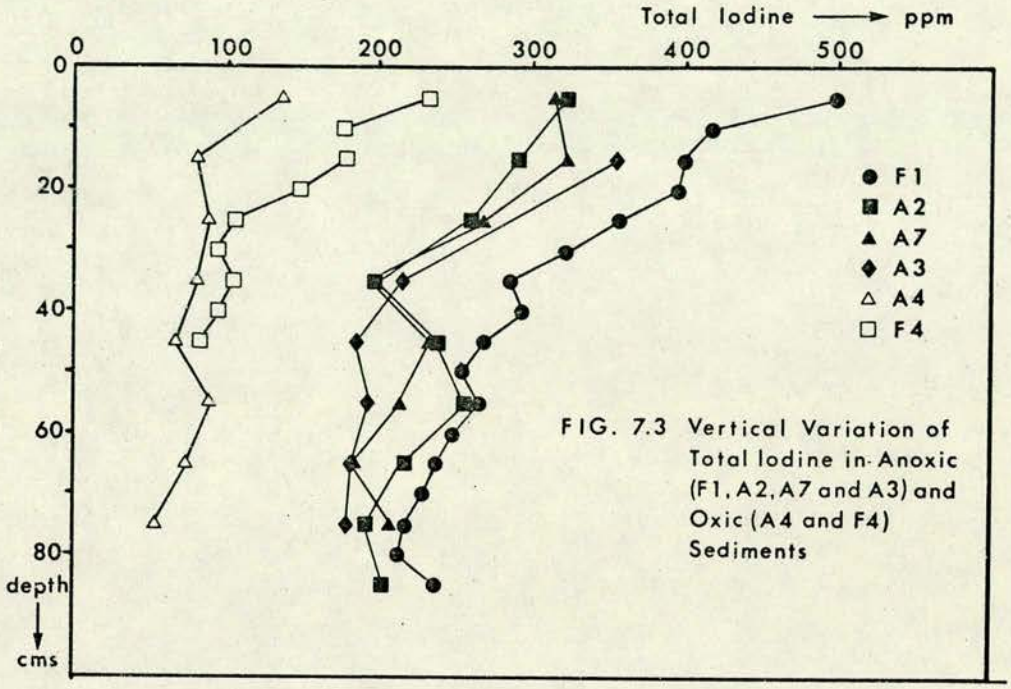
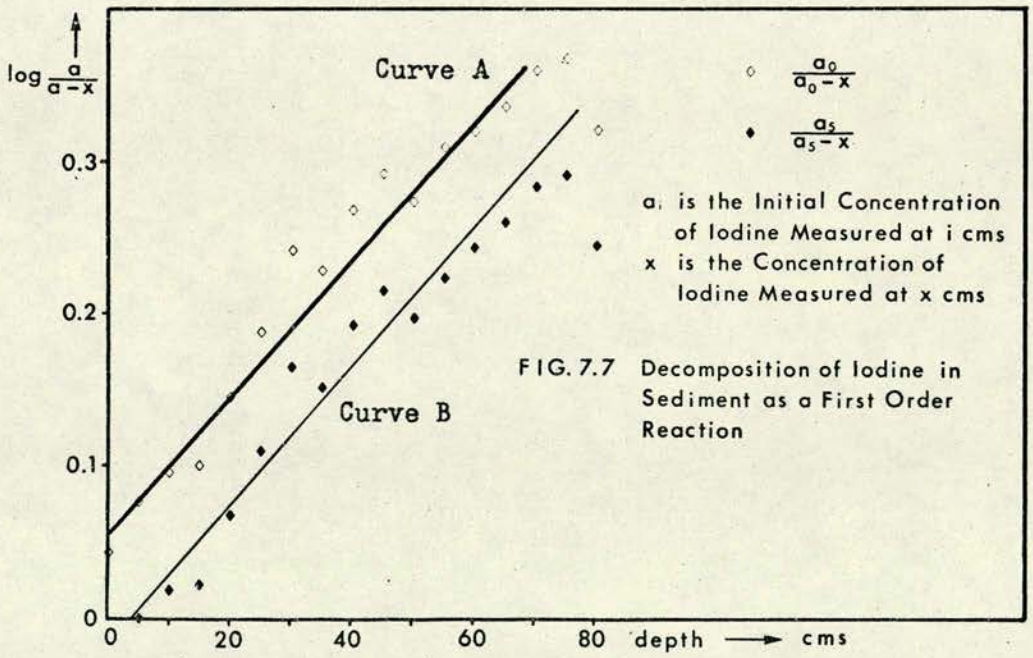


FIG. 7.3 Vertical Variation of Total Iodine in Anoxic (F1, A2, A7 and A3) and Oxic (A4 and F4) Sediments



a_i is the Initial Concentration of Iodine Measured at i cms

x is the Concentration of Iodine Measured at x cms

FIG. 7.7 Decomposition of Iodine in Sediment as a First Order Reaction

iodine with depth, while cores A4, A7, A2 and A3 show a somewhat more complex and less pronounced decrease with depth. Since sediment and pore water geochemistry of basin cores A2, A3, A7 and F1 are very similar, it is suggested that the differences in iodine concentration may be due to over vigorous drying of the sediment samples collected in April 1974. Iodine is a volatile element b.p. = 184°C and it is necessary to be very careful in the drying of sediment prior to analysis, a criticism which can be used against the results of Bojanawski and Paslawski (1970), who heated their samples to 200°C prior to analysis for total iodine.

7.4 Elemental ratios

Three elemental ratios, total organic carbon to total nitrogen (C/N), total organic carbon to total phosphorus (C/P) and total iodine to total organic carbon (I/C) have been calculated in order to provide information on the nature of the organic matter present in the sediment. The C/P and C/N ratios are the weight per cent of TOC divided by the weight per cent of total phosphorus and nitrogen. The I/C ratio is the weight of total iodine in ppm divided by the weight per cent of TOC. The limitations in the use of total nitrogen and particularly total phosphorus as a measure of the organically bound element are discussed above.

The C/N ratio (Table 7 I) of the basin sediments is 10.9 to 15.1 (average 12.6), which is somewhat lower than the ratio in the sediments of Loch Beg, 14.2 - 22.2 (average 16.5). These results are comparable with those found in Oslofjord 7.8 - 16.8 (Doff, 1970), Loch Sunart 7.0 - 15.0 and in the Argentine basin[1] 7.6 - 16.4

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[1] These results are corrected for fixed ammonia in the lattice of aluminosilicates.

(Stevenson and Cheng, 1972).

Figure 7.4 shows an increase of C/N ratio with depth for both the reducing cores 10.9 - 13.9 at the surface to 13.0 - 13.9 at depth and the oxic core from 14.2 - 14.6 at the surface to 16.4 - 16.7 at depth.

The C/P ratio of the basin sediments of Loch Duich is 28.0 - 72.6 with an average of 55.4. This compares to the C/P ratio of 39 ± 4 found in the sediments of the Santa Barbara basin (Sholkovitz, 1973), which he shows to be equivalent to an organic carbon to organic phosphorus ratio of 250 ± 100. The value of C/P ratio found in the sediments of Loch Beg is somewhat lower (33.3 - 48.6) than those of the basin sediments.

Figure 7.5 shows that there is a significant increase with depth in C/P ratio in cores F1 and A2, the two basin cores, which indicates that phosphorus is being lost relative to carbon during sedimentary diagenesis. The oxic core F4 has a somewhat lower C/P ratio (41.3) and shows no recognisable trend with depth.

The I/C ratio $\times 10^4$ for the surface sediments in the basin of Loch Duich (52.8 - 85.1) is significantly greater than the ratio in the surface sediments of Loch Beg (21.7 - 37.1).

The I/C $\times 10^4$ depth profile of the basin core F1 decreases from a surface value of 85.1 to 31.7 at a depth of 80 cms (Fig. 7.6). The form of the curve is very similar to the profile found in the sediments of the Gulf of California (Calvert and Price, 1973), which shows a decrease of I/C ratio $\times 10^4$ from 139 at the surface to a value of approximately 35 at a depth of 2.5 metres. Below this level, the I/C ratio remained relatively constant. In core F1 the initial I/C ratio is

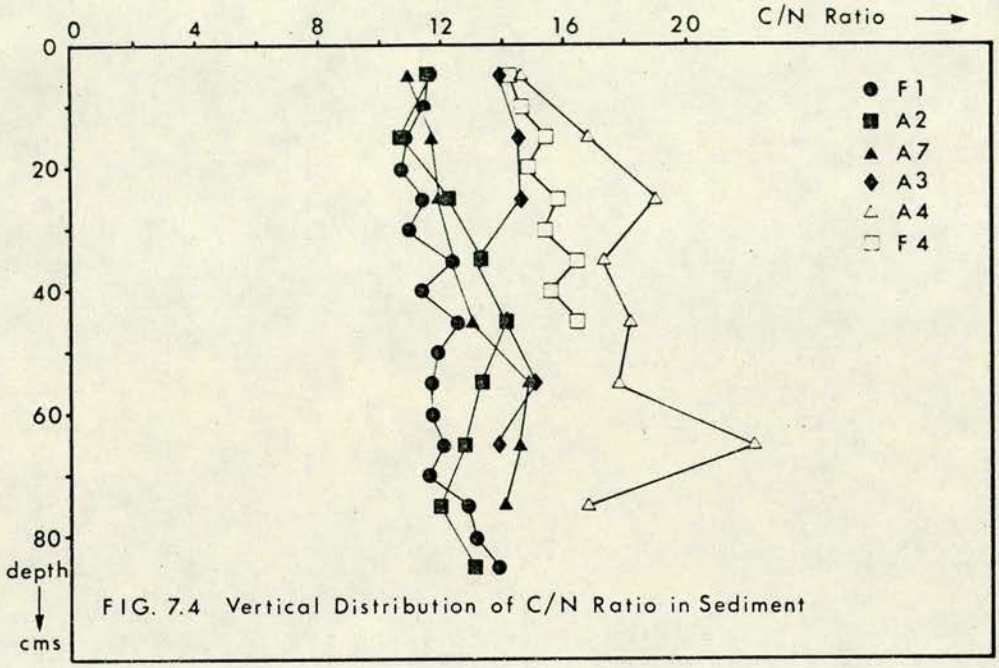

FIG. 7.4 Vertical Distribution of C/N Ratio in Sediment

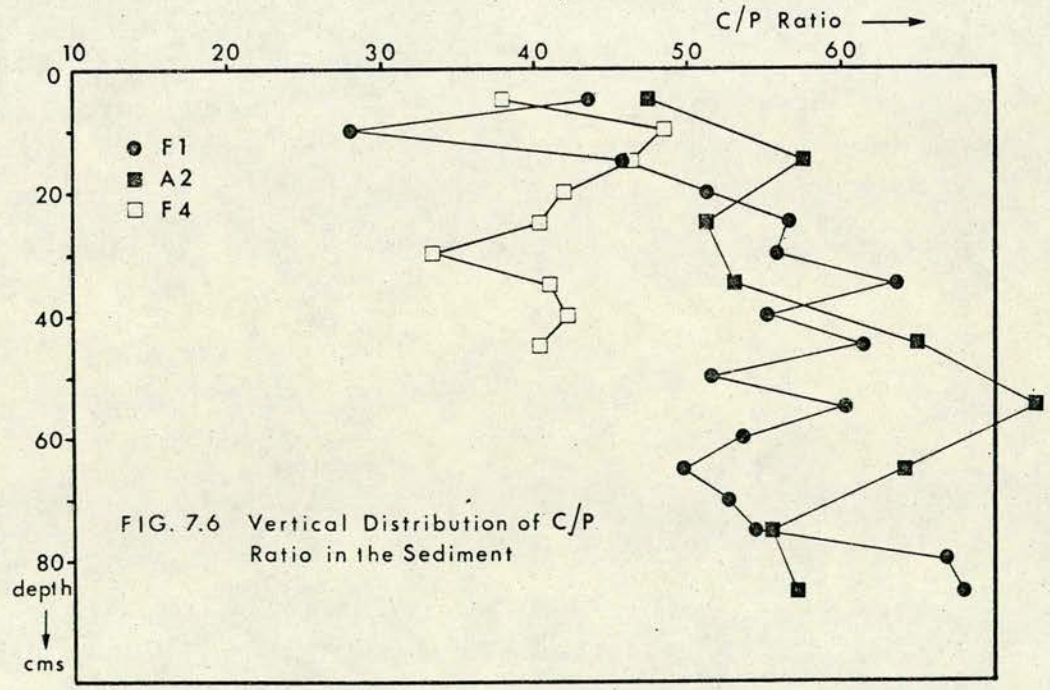

FIG. 7.6 Vertical Distribution of C/P Ratio in the Sediment

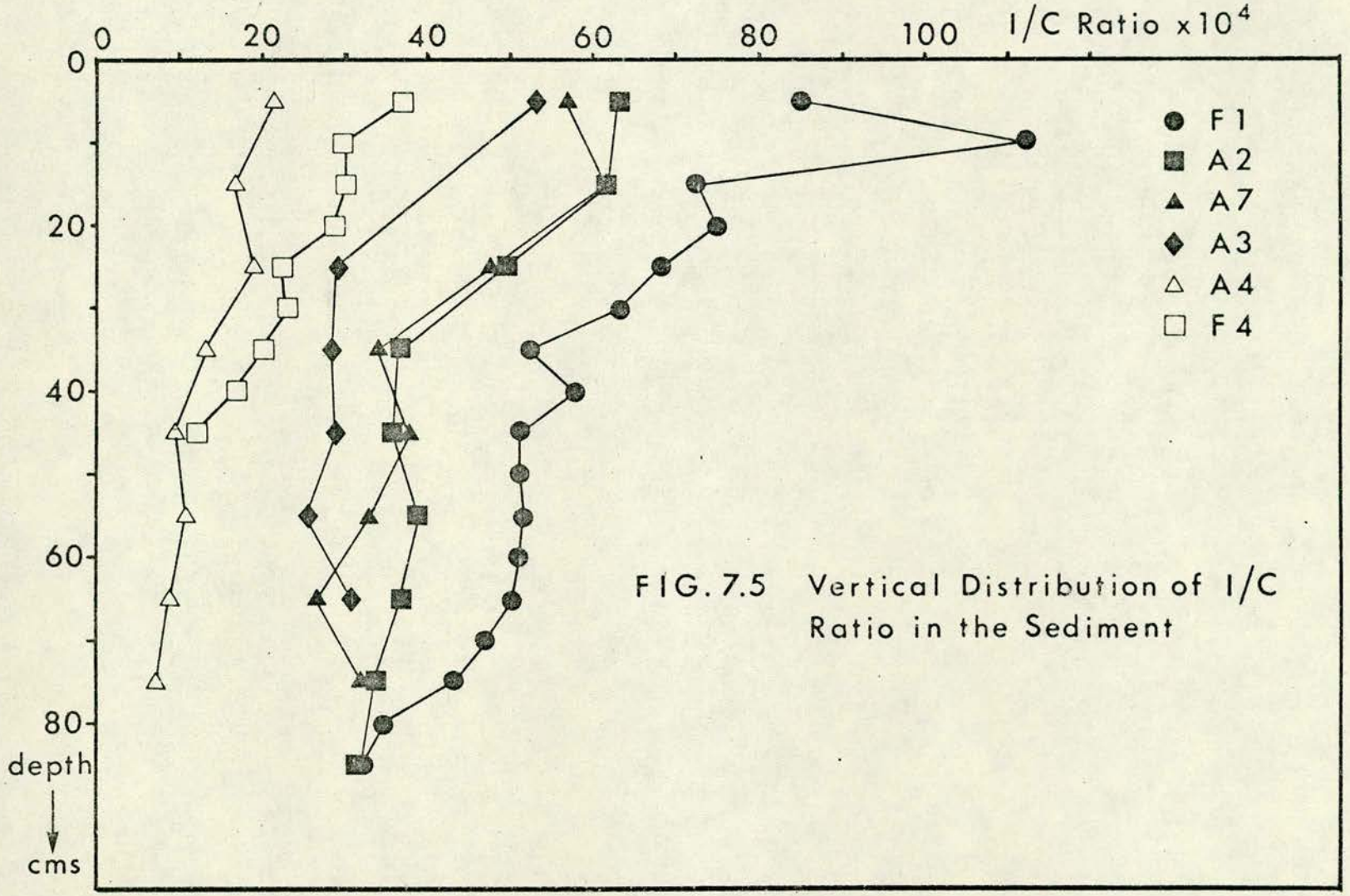

FIG. 7.5 Vertical Distribution of I/C Ratio in the Sediment

lower, due probably to a higher proportion of terrestrial organic matter in Loch Duich, and is not sampled deep enough to have reached the steady state condition that was observed in the Gulf of California sediments. The loss of iodine with depth is interpreted as being due to the diagenetic breakdown of iodine containing organic matter (Shishkina and Pavlova, 1965; Price, 1973). Because of the exponential form of the depth profile for the I/C ratio in the Gulf of California sediments, Price et al. (1970) suggest that this breakdown is first order with respect to the total iodine concentration in the sediment.

In order to examine this conclusion in so far as it applies to the data collected for the basin core F1 of Loch Duich, a plot of $\log_{10} I_o/I_x$ vs. depth[1] was drawn (Figure 7.7), where I_o was taken as the surface concentration of iodine and I_x is the concentration of iodine at a depth x cms. In a true rate equation, the $\log_{10} A_o/A_x$ is plotted against the time of decomposition of A, however in the basin core of Loch Duich it has not been possible to obtain a sedimentation rate (Chapter 3.8) and it is thus necessary to assume that

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[1] For a reaction where $A \longrightarrow B + C$ and the reaction is first order with respect to the decomposition of A then;

$$\log_{10} \frac{A_o}{A_x} = \frac{k}{2.303} t$$

where A_o is the initial concentration of A,

A_x is the concentration of A after time t

and k is the rate constant. (Moore, 1965)

the sedimentation rate has remained constant over the time represented by 80 cms of sediment and thus to use depth as a measure of time.

Figure 7.7 shows the graphical representation of this rate equation for two initial iodine concentrations, I_o equal to the iodine concentration at 0 cms (curve A) and I_o equal to the iodine concentration at 5 cms (curve B). Both curve A and curve B can be represented by straight lines with linear regression coefficients (LRC) of 0.955 and 0.976 respectively. Since this data can adequately be represented by a straight line, it can be inferred that the decomposition of total iodine within the top 80 cms of the basin sediments of Loch Duich can be represented by a first order reaction.

The significant difference between curve A and curve B is that curve A has an intercept on the X and Y axes (intercept = -15.2 on the abscissa), while curve B passes through the origin (intercept = -1.39 on the abscissa). This difference can be explained by noting that the concentration of iodine at depth 0 - 5 cms is anomalously high. The chemical analysis of this sample was repeated and found to be reproduceable. This suggests that this high value is a real phenomenon and is related to the reactions which iodine undergoes close to the sediment-water interface. There is a different reaction rate and possibly also order of reaction within the top 5 centimetres as compared to the remaining 75 centimetres.

7.5 Chemical treatments of the sediment

A number of chemical treatments were performed on the dried sediment to try to separate the sediment into different phases - organics, oxides and humic substances. Details of the methods used

are given in Appendix B. In order to remove all the organic matter, the sediment was boiled with hydrogen peroxide. This treatment also removes all the elements which are free in the pore waters, plus an unknown fraction of the loosely adsorbed elements. In the second treatment, the sediment was extracted with a sodium dithionite - sodium tricitrate reagent buffered to pH = 7.8 with sodium bicarbonate (Mehta and Jackson, 1960). This is a mild reducing agent which is known to remove iron oxides from soils and clays while leaving the iron silicates untouched. No previous data was found on the effect of this reagent on organic matter. Data is given below on this problem. The hydroxylamine reagent, which is often used to remove oxides from sediments of all types, was not used because it is known that it removes a large fraction of the iron which is bound to organic matter (Chester and Hughes, 1967). Therefore, before this chemical treatment can be used on recent coastal marine sediments which are comparatively rich in organic matter (Foster and Hunt, 1975), much more data on the effect of this treatment on the organic matter is required.

In order to remove "humic" substances from the sediment, a sodium pyrophosphate treatment (Schnitzer and Kahn, 1972) was used. This is a relatively mild extraction procedure, which is known to give a good extraction of humics from soil samples.

Table 7 II shows the results of analyses of core F1 , a reducing basin core for carbon, nitrogen and iodine, using these three chemical treatments. There are no results for carbonate carbon for sediment after the peroxide treatment because insufficient sample remained for analysis. Two values for the % organic carbon remaining

Table 7 II .

Concentration of organically associated elements (Core F1) after chemical treatments (in wt. %)

Organic Carbon (except (1) which is Total Carbon)

Depth (cms)	Untreated	Dithionite treated	Pyrophosphate treated	Peroxide (1) treated
0	5.22	3.95	3.34	1.58
5	3.64	3.87	3.01	1.08
10	5.03	3.82	3.45	0.90
15	5.14	4.07	3.50	1.07
20	4,80	4.32	3.50	1.53
25	5.01	3.97	5.22	1.64
30	5.07	4.41	3.53	1.99
35	4.96	4.03	3.20	0.79
40	4.91	3.83	3.34	1.77
45	4.88	3.30	3.46	1.80
50	4.81	4.10	5.21	1.98
55	4.81	3.97	3.08	1.53
60	4.46	4.07	3.03	1.58
65	4.74	3.94	3.12	1.52
70	4.89	4.75	3.61	1.83
75	6.01	4.98	-	-
80	6.79	5.45	5.11	2.20
Average		79%	70%	11%(2) 31%(3)
S.D.		9%	13%	9% 7%

Total Nitrogen

Depth (cms)	Untreated	Dithionite treated	Pyrophosphate treated	Peroxide treated
0	0.45	0.38	0.32	0.07
5	0.32	0.38	0.35	0.02
10	0.46	0.34	0.30	0.02
15	0.48	0.39	0.37	0
20	0.42	0.36	0.35	0.03
25	0.46	0.42	0.48	0.07
30	0.41	0.34	0.31	0.04
35	0.44	0.37	0.33	0.26*
40	0.39	0.25	0.29	0
45	0.41	0.32	0.31	0.09
50	0.41	0.35	0.38	0.06
55	0.41	0.34	0.32	0.04
60	0.37	0.40	0.28	0.02
65	0.41	0.34	0.29	0.05
70	0.38	0.34	0.30	0.05
75	0.46	0.41	-	-
80	0.49	0.40	0.47	0.05
Average		86%	79%	10%
S.D.		12%	10%	6%

continued

Table 7 II (continued)

Depth (cms)	Untreated	Dithionite treated	Pyrophosphate treated	Peroxide treated
Total Iodine (in ppm)				
0	498	134	156	0
5	417	181	217	7
10	399	125	41	7
15	395	218	228	8
20	356	192	196	3
25	323	181	175	19
30	285	128	144	16
35	294	159	183	0
40	268	170	173	8
45	254	139	146	15
50	265	154	162	7
55	249	133	148	8
60	238	209		14
65	229	134	133	7
70	217	144	119	25
75	213	163	134	
80	237	129	131	13
Average		55%	53%	3.5%
S.D.		15%	14%	2%

* anomalous value, not included in average.

after chemical treatment are thus given; the first value is the % organic carbon remaining assuming that all of the carbonate remained after peroxide treatment (a minimum value of the organic carbon remaining), while the second value assumes that all the carbonate was evolved (the maximum value for the organic carbon remaining). The true value will be between these two, depending on the amount and nature of acid liberated during the oxidation process.

The results show that the treatment with hydrogen peroxide removed almost all the nitrogen (93%) and iodine (97%) as well as a very large proportion of the organic carbon (70 - 89%). This shows that within experimental error all the iodine in the sediment is organically bound, confirming the conclusions of Shishkina and Pavlova (1965) and Price (1973). Nitrogen is known to be present in sediment as both an organic phase and in the form of ammonium ions within the inorganic phase. Both these fractions are oxidisable, and hence it is not possible to use hydrogen peroxide to differentiate between them.

The pyrophosphate treatment removed an average of 47% of the iodine, 30% of the total organic carbon and 20% of the total nitrogen. These averages represent the proportion of the sedimentary organic matter which is present in the humic fraction. The fraction of TOC (30%) present in the humic fraction compares with 10 - 35% found in sediments of the California borderlands (Nissenbaum and Kaplan, 1972), 44% in the sill sediments of Saanich Inlet (Brown et al., 1972), 8 - 20% in Black Sea sediments (Bordovskiy, 1965) and 17 - 40% in sediments from the Bering Sea (Bordovskiy, 1965).

Although the dithionite is only a mild reducing agent,

nevertheless a significant proportion of the organic matter was removed from the sediment by this treatment; 15% of the total nitrogen, 45% of the total iodine and 22% of the total organic carbon. No information is known about the nature of the organic matter removed by this treatment, and thus this suggests that the use of reducing agents as a measure of the oxide phase in organic rich sediments is strictly limited.

7.6 Organic content of the sediments of Loch Duich

The sediments of Loch Duich are organic rich and thought to be typical of recent coastal marine sediments. The organic carbon content, which is the usual measure of total organic matter, is typical of the range found in other fjords (1 - 9%), being greater than values found on the open shelf (2 - 5%) and much greater than those found in ocean sediments ($\sim$1%).

The nature of the organic matter in so far as it has been investigated in the sediments of Loch Duich is also closely comparable with values found in other coastal marine sediments. Thus the C/N ratios, I/C ratios, C/P ratios and proportion of "humic" fraction to TOC are all within the range of values found by other workers in similar environments.

The nature of the organic matter in Loch Beg as compared to that in Loch Duich

It is noted that although the average TOC of the cores collected from Loch Beg (5.8%) is similar to that of the basin cores (5.5%), there is considerable evidence that the nature of the organic matter is different.

The proportion of pyrophosphate extractable humics is higher

(42%) in the Loch Beg samples than for the basin sediments (11 - 30%). The C/N ratio is higher for Loch Beg sediments (16.5) than for basin cores, while the I/C ratio for the surface sediments is lower (21.7 - 37.1) against (52.8 - 85.1). These differences in elemental ratios can be explained by a higher proportion of terrestrially derived organic matter in the sediments of Loch Beg as compared to those in the central basin of the Loch. Typical C/N ratios for a coastal marine sediment are between 9.3 - 14.4 (Sholkovitz, 1973). This is in the range of those found for the basin cores of Loch Duich. By contrast, the C/N ratio of soil humic acids ranges from 13.8 - 35.3 (Schnitzer and Kahn, 1972), while Manskaya and Drozdova (1968) give the typical C/N ratio for humic acids derived from peat to be 14.3, these values being comparable to the average C/N ratio of the Loch Beg samples of 16.5.

Bowen (1966) gives an average iodine content for living tissue which shows that terrestrial plants have a lower iodine content (0.4 ppm in angiosperms) than marine plants (300 ppm in phytoplankton, 1500 ppm in brown algae). In addition, Mun and Bazilevich (1964) show that organic matter in lake sediments does not absorb iodine as efficiently from the surrounding water as do marine organics, a possible mechanism postulated by Price and Calvert (1973a) to explain the very high I/C ratios observed in surface sediment samples. Price et al. (1970) and Price and Calvert (1973a) show that there is an increase in I/C ratio in surface sediments with distance from shore in both the Barents Sea and off S.W. Africa, and conclude that this is due to dilution by terrestrially derived organic matter in the nearshore region.

Thus it is suggested that the observed differences in elemental ratio between Loch Beg and Loch Duich are due to the presence of a higher proportion of terrestrially derived organics. This organic matter may be in part the product of the flocculation of terrestrially derived humic acids on contact with sea water (Sholkovitz, 1976). A small proportion of this flocculant had been observed as particulate matter floating above the picnocline. However, because of the small density gradient across the picnocline and the high degree of tidal mixing, it is thought likely that most of this flocculant will have been removed in the immediate vicinity of the outflow of the river.

Relation between organic matter in the sediment and metabolic processes observed in the pore waters

It can be seen from depth profiles of TOC in both oxic and anoxic cores that there is no simple relationship between the TOC and the metabolic processes which take place within the sediment. Alkalinity, ammonia, phosphate and dissolved organic matter (DOM) all accumulate in a pseudozero order manner (i.e. they increase linearly with depth) within the sediment. Although it is known that these dissolved species are derived from the decomposition of sedimentary organic matter, it is not possible to measure directly the loss of solid sedimentary organics. One of the reasons for this is that very small changes in the concentration of sedimentary organics can result in very large changes in pore water chemistry. Table 7 III shows the change in concentration of the principal species containing C, N and P in the pore waters of a reducing core. Assuming that there is no diffusion of these species out of the pore waters, then

Table 7 III

Change in the concentration of C, N and P in the pore waters relative to the necessary change in the organic content of the solid fraction
(No account is taken of alteration in organic flux to the sediment nor of diffusion)

Core	depth (cms)	element in pore waters	Conc. in sediment	element in pw / conc. in sediment x 100%
A3	60	HCO_3^- = 32mM	5%	0.8%
A2	70	HCO_3^- = 50mM	5%	1.2%
A3	60	DOC = 46ppm	5%	0.1%
A2	70	DOC = 39ppm	5%	0.1%
A3	60	NH_4^+ = 2.3mM	0.4%	0.8%
A2	70	NH_4^+ = 3.3mM	0.4%	1.2%
A3	60	PO_4^{3-} = 150µM	0.1%	0.5%
A2	70	PO_4^{3-} = 205µM	0.1%	0.7%

the change in sedimentary organic matter is calculated equivalent to the observed accumulation of dissolved species in the pore waters. From this calculation it can be seen that all the observed changes in pore water chemistry could be derived from a decrease in the measured organic carbon of 1%, total nitrogen 0.5% and total phosphorus 1%, changes which are well within the analytical error. Thus any attempt to relate the production of these dissolved species directly to the total concentrations of these elements in the sediment fails because carbon, nitrogen and phosphorus in the sediment only contain a small proportion which is metabolised and removed as dissolved species, the remainder behaving as refractory organic matter or being present as an inorganic phase.

Berner (1974) has used the concept of potentially metabolizable organic matter (MOM) in order to relate the breakdown of sedimentary organic matter to the production of dissolved species, NH_4^+, PO_4^{3-}, SiO_2 and S^{2-}.

He assumes that this organic matter decomposes at a first order rate and hence that the concentration of metabolizable organic matter decreases exponentially with depth within the sediment. Berner uses the decrease of total organic matter (carbon and nitrogen) with depth in sediments in the Santa Barbara basin as a measure of MOM. However, it is possible to interpret this decrease in organic matter as being due to an increase in the recent flux of organics to the sediment rather than due to diagenetic decomposition. The values for total organic carbon (TOC) and total nitrogen (TN) in the Santa Barbara basin (Rittenberg et al., 1955; Sholkovitz, 1973) fluctuate with depth and do not show a smooth exponential decrease as might be expected from a diagenetic change. As is shown above, the

quantity of TOC and TN required to produce all the dissolved nutrients is only ~1% of the total organic matter available in the sediment, and hence TOC is likely to be a poor measure of MOM. In addition, in Loch Duich there is evidence of uniform sedimentary input over the depth of sedimentation being considered (Chapter 3) and an accumulation of nutrients in the pore waters similar in magnitude to that found in the Santa Barbara basin (Sholkovitz, 1973), and yet there is no systematic trend measurable in TOC. It is thus concluded that it is not possible to obtain a measure of MOM directly from TOC or TN.

However, I is an element which, unlike N and P, is known to be entirely bound to organic matter and which decreases exponentially with depth. This suggests that all the I is involved in a diagenetic decomposition, unlike C which has a large refractory component. Total sedimentary iodine could thus be used directly as a measure of MOM. Unfortunately, although it is known that iodine accumulates in the pore waters of recent sediments (Shishkina and Pavlova, 1965; Bojanowski and Paslawski, 1970), no complete profiles of sediment and pore water iodine from the same core exist, and it is thus not possible to perform a kinetics calculation on the sedimentary iodine - pore water iodine system.

Recycling of iodine in the top metre of the sediment

The observed geochemistry of iodine in the top metre of recent sediments, such as those in the basin of Loch Duich, can best be explained by a recycling mechanism (Figure 7.8).

Iodine is removed from sediment by a first order diagenetic process and must be transferred to the pore waters. This

(I/C ratios are $\times 10^4$)

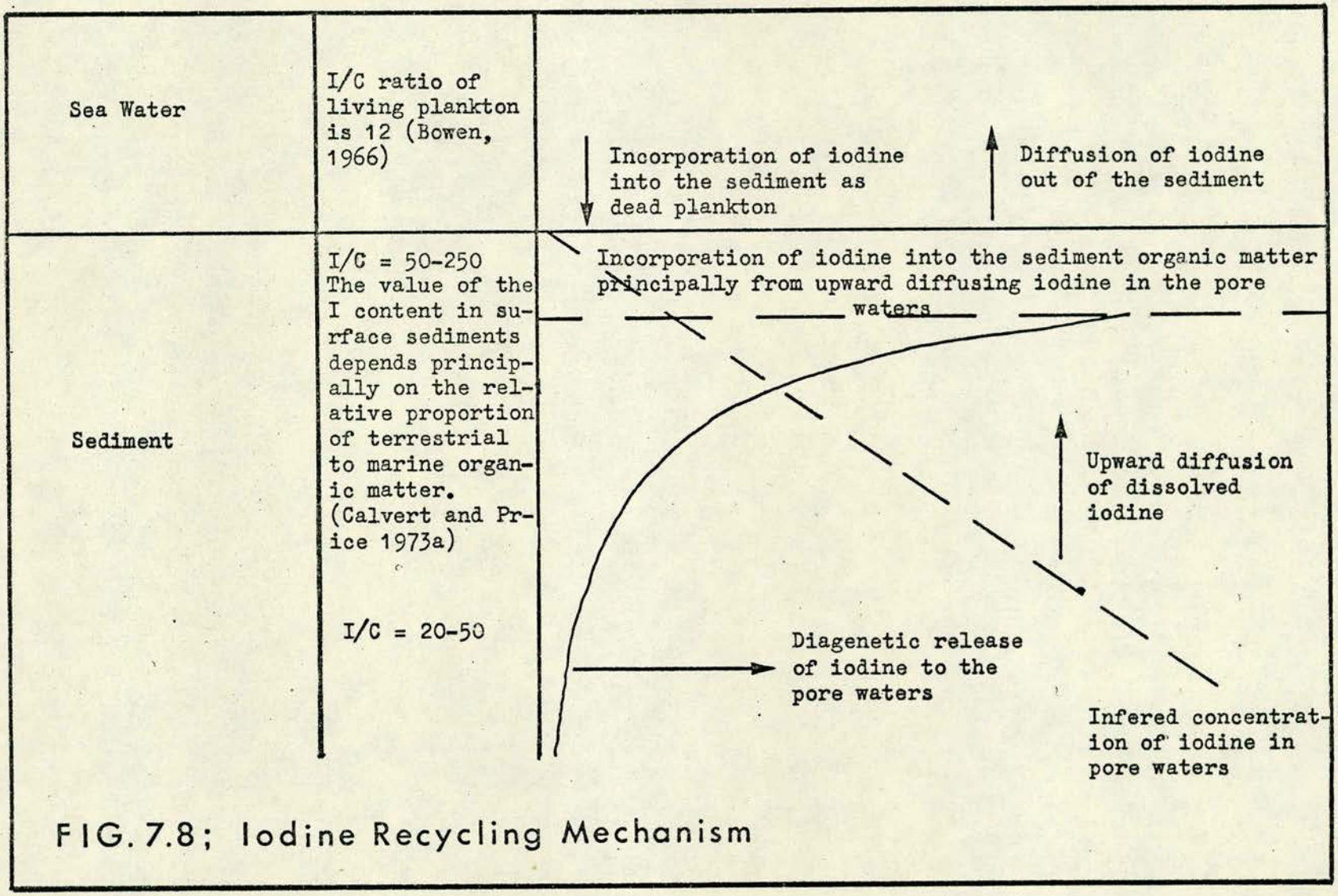


FIG. 7.8; Iodine Recycling Mechanism

accumulating dissolved iodine is likely to be far in excess of the concentration of iodine in the overlying sea water, and thus an upward diffusion gradient is set up. Similar diffusion gradients in the pore waters also exist for DOC, dissolved nutrients and the trace metals iron, zinc and copper.

Price (1973) notes that the initial concentration of iodine in the sediment is much greater than is possible by the simple accumulation of dead plankton; the I/C ratio $\times 10^4$ in living plankton is 12 (Bowen, 1966), while the I/C ratio $\times 10^4$ in recent sediments is 50 - 250.

This enrichment of the surface sediments in iodine has been interpreted as being due to the preferential loss of carbon in the water column. It is, however, difficult to explain why carbon is lost preferentially in the water column, while iodine is lost preferentially in the sediment. A more likely explanation is that this enrichment of iodine is caused by the removal and precipitation of upward diffusing dissolved iodine by microbial action in the surface layers of the sediment. This results in a recycling process being set up similar to that postulated to be controlling the distribution of certain trace metals in the upper layers of the sediment (Chapter 9).

CHAPTER 8

TRACE METALS IN INTERSTITIAL WATERS OF LOCH DUICH

8.1 Introduction

The pore water geochemistry of the trace metals Mn, Fe, Cu and Zn has previously been investigated in reducing sediments from the California borderlands (Brooks et al., 1968), Saanich Inlet (Presley et al., 1972) and Loch Fyne (Duchart et al., 1973). In all of these studies the concentration of trace metals greatly exceeds that of the overlying sea water, often by an order of magnitude or more. A surface excess of dissolved Mn was found in those cores where the oxic - anoxic redox boundary was close to the sediment - water interface. However, there was no recognisable trend for dissolved Fe, Cu and Zn. These interstitial waters also contain up to 2 mMoles of dissolved sulphide, which should reduce the concentration of these dissolved metals below that of the overlying sea water because of the extreme insolubility of the trace metal sulphides (Brooks et al., 1968). The concentration of DOM in anoxic pore waters is also greatly in excess of that in the overlying sea waters (Nissenbaum and Kaplan, 1971; this study) and furthermore this DOM contains a proportion of humic and other fractions which are known to be strongly associated with certain trace metals. Additionally, a significant proportion of trace metals in sea water are bound to organic matter (Slowey et al., 1967; Williams, 1969; Foster and Morris, 1971), although the details of the chemistry of these interactions are not known. It was thus suggested that the solubility of these trace

metals and particularly Cu, Fe and Zn in anoxic pore waters is controlled by DOM (Presley et al., 1972; Duchart et al., 1973).

The purpose of this study is to investigate the speciation of trace metals in sediment pore waters, particularly in relation to organic matter, and then to apply this knowledge to the observed geochemistry of these trace metals in the sediment.

The total concentration of trace metals (Mn, Fe, Cu and Zn) was measured in the interstitial waters from Loch Duich and related to those parameters which are thought to be possibly important in controlling their solubility; total DOC as an estimate of organic matter, dissolved sulphide and nutrients which are associated with characteristic values of pE and pH. Attempts were made to correlate these changes with fluctuations in trace metal profile.

In addition, attempts were made to analyse directly the trace metals which are bound to organic chelates. Three such experiments were performed in which:

1) The pore waters were analysed before and after oxidation for trace metals, the difference being a measure of strongly bound trace metals.
2) The pore waters were ultrafiltered to separate HMW and LMW fractions, and each of these fractions was analysed for trace metals and DOC.
3) The pore waters were acidified and the resulting humic acid precipitate was analysed for trace metals.

8.2 Method of sampling, storage and analysis

The experimental procedures used in the sampling, storage and analysis of the pore waters are set out in a flow chart (Figure B.1).

It is necessary to present these procedures in some detail because the analysis of trace metals and organic matter is particularly sensitive to alteration and contamination during handling and storage.

The sediment samples were collected using a 4-inch diameter gravity corer. The sediment core was recovered in a plastic core liner, which was capped and stored upright at ambient temperature (0 - 10°C) while the remaining cores were collected. They were then transported by van to Edinburgh overnight, the maximum time between sampling and the cores being placed upright in the cold store at 5°C was 48 hours. The sediments were then squeezed mechanically to extract the pore waters by the method of Kalil and Goldhaber (1973). All the cores were squeezed within 48 hours of arrival at the laboratory, filtered through 0.45 μ Sartorius filters and, after the first few mls were discarded (Troup et al., 1974), subsamples of pore water were removed for the analysis of sulphide, dissolved organic carbon and titration alkalinity. The remainder was placed in acid-cleaned polythene bottles and stored untreated in the cold store at 5°C until required for combination and analysis.

The nature of the conditions of storage (i.e. temperature and additives) depends on the type of analysis planned. In this case, the pore waters were to be analysed for both trace metals and organics. It was considered unwise to freeze the pore waters, since this is known to precipitate organic matter out of solution (Barsdate and Matson, 1966). Acidifying pore waters to pH = 2 resulted in the formation of a brown flocculant which is humic in nature. This flocculant was analysed for its trace metal content by an XRF emission technique (Price and Calvert, 1973) and found to contain

significant quantities of Fe (8 - 20 ppb measured relative to the total concentration of dissolved Fe in the pore waters). On the basis of these results, it was decided not to acidify the pore waters if they were to be analysed for Fe and DOC, thus the pore waters were left untreated. On storage, brown lozenge shaped crystals formed in the bottom of the untreated samples. These were filtered out of the pore waters and analysed chemically and spectroscopically. The results of an X-ray diffraction and infra-red spectroscopic analysis showed that this precipitate is calcite; a similar observation on stored pore waters has been made by Berner et al. (1970). The crystals were also analysed for their trace metal content by atomic absorption spectroscopy and found to contain 0.6 - 1.0 ppb Mn, 2.2 - 4.3 ppb Fe, 1.1 - 2.5 ppb Zn and 0.6 - 0.9 ppb Cu. The values are low compared to the total concentrations of trace metals in the pore waters and no correction was made.

Because each trace metal analysis required a minimum of 80 mls of interstitial water, and samples were analysed for trace metals both before and after oxidation, it was necessary to combine samples from two or more cores collected simultaneously from the same locality. It was decided to combine the pore water samples on geochemical criteria. A complete depth profile of titration alkalinity was measured for each core; a typical set of profiles is given in Figure 8.2 for cores A7A and A7B. The pore waters were then combined on the basis of the best geochemical fit; A7B was combined with A7A with a relative displacement of 10 centimetres, thus A7B10 was combined with A7A0, A7B20 with A7A10, etc. Of the other sets of cores, those collected from stations A4, F4, A2 and F1 were combined with no

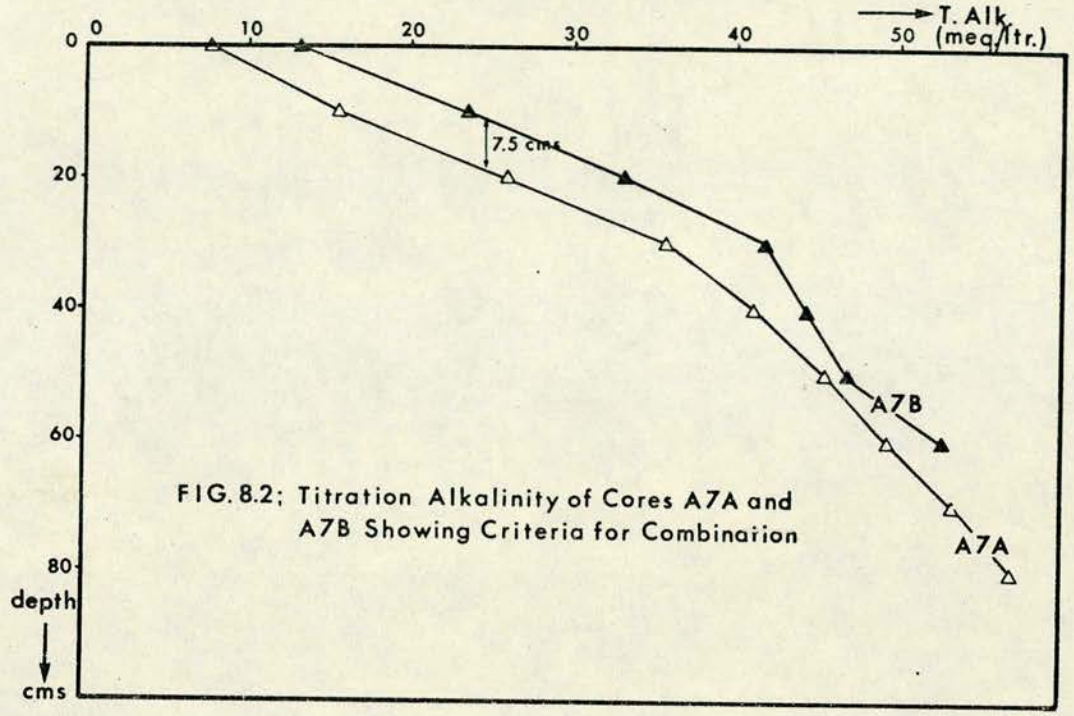


FIG. 8.2; Titration Alkalinity of Cores A7A and A7B Showing Criteria for Combination

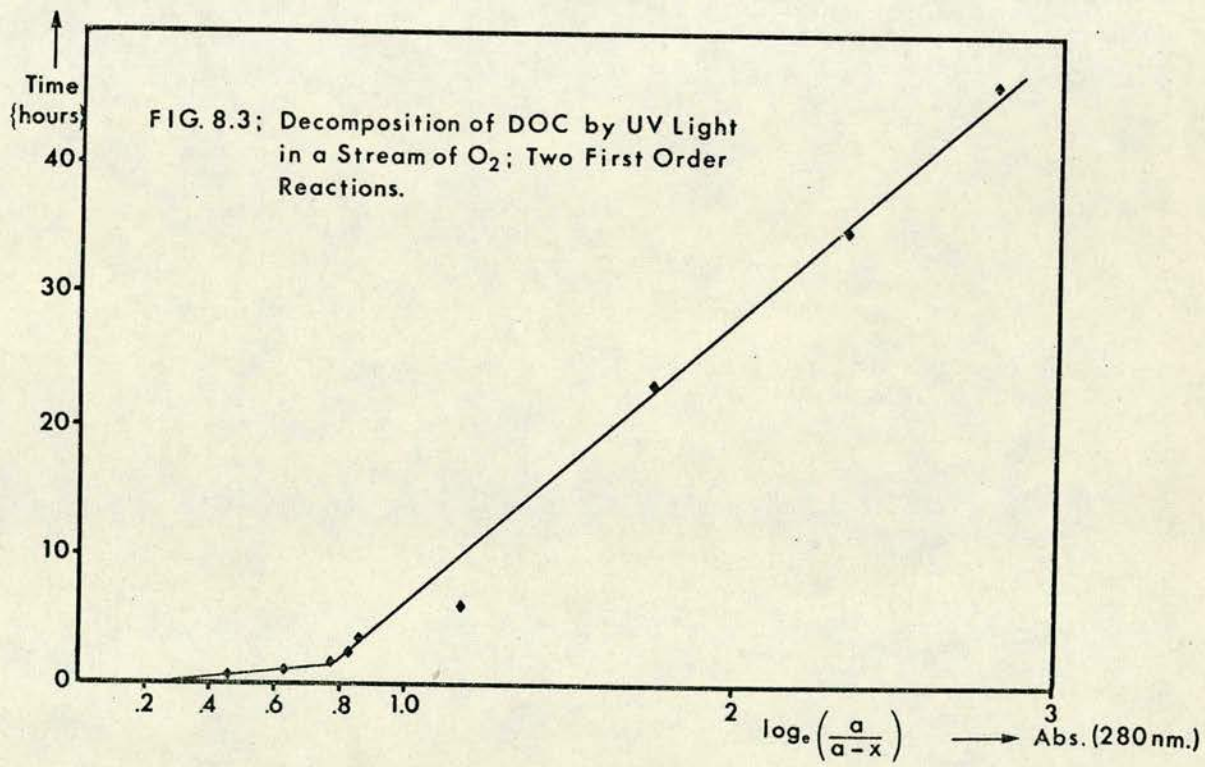


FIG. 8.3; Decomposition of DOC by UV Light in a Stream of O_2; Two First Order Reactions.

displacement, while A3B was combined with A3A with a displacement of ten centimetres.

The method used for the analysis of trace metals (Cu, Fe, Zn and Mn) in pore waters was based on the DEDTC-MIBK extraction method of Duchart et al. (1973). Details of the method are given in Appendix B. Using the method of standard additions, a complete set of results for Cu, Fe, Zn and Mn were obtained. Preliminary experiments were performed to analyse the pore waters for Pb, Ni, Cd and Co. However, all of these elements were present in too low concentrations to allow satisfactory analyses to be accomplished.

Estimation of analytical errors in the analysis of trace metals

It was not possible to estimate errors by a simple duplication of a single sample, because there was insufficient pore waters available. However, the method of standard addition is in a sense four replicates of a single sample. Thus error values were calculated by taking eight samples chosen at random and graphically producing the highest and lowest value compatible with the data available. These values were compared with the value which had been taken to be the result of the analysis. The mean values of the errors in the analysis of these four trace metals in pore waters were;

Manganese	$\pm$ 10%
Iron	$\pm$ 10%
Zinc	$\pm$ 30%
Copper	$\pm$ 45%

It is suggested that the stated errors for the analysis of trace metals in saline waters by similar AA techniques such as the $\pm$ 5% for copper, $\pm$ 10% for zinc for anoxic pore waters claimed by

Presley et al. (1972), the $\pm$ 6% for copper and $\pm$ 2% for iron claimed by Taylor (1974) for sediment interstitial waters or $\pm$ 7% for copper and $\pm$ 2% for zinc in sea water (Duinker et al., 1974) are overly optimistic.

Because of the very low concentrations of metals present in the pore waters, very great care was taken in the handling of samples to avoid contamination. All glassware was acid cleaned between each analysis and then washed three times with freshly distilled deionised water.

A sample of the pore waters was removed for oxidation to destroy all the trace metal - organic chelates. 100 mls of pore water was subsampled, acidified to pH = 2 with aristar hydrochloric acid and irradiated with an ultraviolet light (100 W) in a stream of oxygen for 24 hours. The details of the experimental procedure are given in Appendix B. To check the completeness of oxidation and the nature of decomposition, a run was performed with subsamples of pore waters being removed at fixed time intervals. The DOC content of these subsamples was then obtained by measuring the absorbance at 280 nm. The results of this experiment are shown in Figure 8.3. There are at least two reactions occurring, both first order with respect to the concentration of DOC: an initial reaction which causes the rapid breakdown of approximately 50% of the DOC in the first 90 minutes and a slower reaction which causes the removal of the remaining DOC. In all the samples which were oxidised as an additional check that oxidation was complete, the absorbance (280 nm) was compared before and after oxidation. In all cases it was found to have been reduced to $<1\%$ of its initial value.

The details of the theory and the practical techniques for the ultrafiltration of pore waters are given in Chapter 6.4. It is assumed that only trace metals bound to high molecular weight organic and inorganic matter will be retained behind the ultrafilter in the retentate and that all the ionic metal or metal bound to low molecular weight complexes will pass through the ultrafilter. The ammount of trace metals in the proportion of pore waters which passed through the ultrafilter (the ultrafiltrate) ($m_u \mu g$) was measured by standard addition on four subsamples each of volume (v_u mls). The small volume of pore water (v_r mls) which was retained behind the ultrafilter (the retentate) and which contained all the high molecular weight material was analysed as a single sample and the standard addition calibration line for the corresponding ultrafiltrate was used to calculate the ammount in the retentate ($m_r \mu g$). The measured concentration of the retentate is somewhat less reliable than that for the analysis of the ultrafiltrate because of this method of analysis. The mass of the ultrafiltrate (x_u grms) and the retentate (x_r gms) was measured. A series of calculations was performed to obtain the concentration of metal bound in the high molecular weight fraction of the original sample (C_{HMW}), the concentration of metal present in low molecular weight fraction of the original sample (C_{LMW}) and the % bound in the high molecular weight fraction when compared to the total concentration of metals in the pore waters. The generalised results of these calculations are,

$$C_{HMW} = \left(\frac{m_r}{v_r} - \frac{m_u}{v_u} \right) \cdot \frac{x_u}{x_u + x_r}$$

$$C_{LMW} = m_u / v_u$$

$$\% \text{ bound} = \left(\frac{C_{HMW}}{C_{HMW} + C_{LMW}} \right) \times 100\%$$

8.3 Results

Dissolved trace metals in sea water

The profiles of trace metals in the water column of Loch Duich above coring stations A7, A2 and A4 were measured. The results are shown in Table 8 I. These show that trace metals in Loch Duich were vertically homogeneous, probably because the water column was well mixed at the time of sampling (see temperature, salinity and oxygen measurements in Chapter 4). The concentration ranges of trace metals were: Mn 0.7 - 4.4 ppb, Fe 0.9 - 8.5 ppb, Zn 1.4 - 8.2 ppb (ignoring the anomalously high surface sample at station B7) and Cu 0.3 - 3.3 ppb. These values compare closely with concentrations of trace metals found in the North Sea (Dutton et al., 1973) of Mn 0.7 - 15.9 ppb, Fe 0.5 - 18.4 ppb, Zn 0.8 - 12.0 ppb and Cu 0.3 - 2.0 ppb and to the "average" sea water concentrations of Mn 2 ppb, Fe 10 ppb, Zn 10 ppb and Cu 3 ppb (Goldberg, 1965).

Dissolved trace metals in sediment pore waters

Six cores were analysed for trace metals, five of these cores, F1, F4, A4, A7 and A2 were ultrafiltered and the total trace metal quoted is the value obtained by calculation from the ultrafiltrate and retentate (see above), while core F1 was also analysed for total trace metal prior to ultrafiltration. Table 8 IV shows the comparison between the total metal measured directly and the total metal calculated from the analysis of the ultrafiltrate and retentate. The

Dissolved trace metals in pore waters of sediments from Loch Duich

Key to terms

(1) HMW fraction is the concentration of trace metals in the HMW fraction of the total pore waters

(2) LMW fraction is the concentration of trace metals in the LMW fraction of the total pore waters

(3) Total calc. is the sum of the HMW and LMW fractions.

(4) % Bound is the concentration of trace metal in the retentate divided by the total calculated trace metal concentration (x100%).

(5) Total meas. is the total concentration of trace metals measured directly.

(6) % Bound is the concentration of trace metal calculated to be in the HMW fraction (Total meas. - LMW fraction) divided by the total measured trace metal concentration (x100%).

Table 8 I

Dissolved trace metals in the sea water of Loch Duich in ppb

Station and depth (mtrs)		Mn	Fe	Cu	Zn
B7	0	2.2	3.8	1.9	20.1
	5	0.9	4.7	1.0	6.7
	20	1.3	3.6	1.1	2.1
	30	1.4	2.9	0.9	5.7
	40	1.8	4.4	0.8	3.3
	60	1.4	0.9	0.3	1.4
	75	4.4	4.9	0.6	1.8
	80	2.6	4.3	0.3	1.8
B1	5	1.4	2.2	1.7	3.9
	15	1.4	2.9	3.3	4.8
	20	1.4	3.7	1.4	5.1
	30	0.7	6.5	0.4	2.9
	80	0.7	3.2	0.4	1.5
	100	1.6	8.5	1.7	4.3
B4	0	1.6	1.4	0.8	8.2
	10	1.1	2.1	0.8	3.6
River S*		0	22	1.0	49

* A peaty Scottish river similar to the rivers which flow into Loch Duich.

Table 8 II

Dissolved trace metals in the anoxic core A2 in ppb

Depth (cms)	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
5	4500 *	9000	13500	33%
15	11	880	891	1%
25	16	200	216	7%
35	9	33	42	21%
45	6	55	61	10%
55	2	33	35	6%
65	8	47	56	14%
75	2	45	47	4%
IRON				
5	25	26	51	48%
15	53	17	70	76%
25	23	21	44	52%
35	37	12	49	76%
45	34	27	61	56%
55	24	37	61	39%
65	60	20	80	75%
75	19	49	68	28%
COPPER				
5	13	13	26	51%
15	20	6	26	77%
25	10	10	20	50%
35	14	8	22	62%
45	5	2	7	71%
55	8	4	12	67%
65	21	4	25	84%
75	8	6	14	57%
ZINC				
5	43	380	423	10%
15	15	83	98	16%
25	23	47	70	24%
35	26	7	33	79%
45	2	8	10	71%
55	8	8	16	50%
65	38	9	47	81%
75	10	17	27	37%

* analytically suspect result

Table 8 III

Dissolved trace metals in the anoxic core A7 in ppb

Depth cms	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
15	34	693	727	5%
25	2	207	209	1%
35	4	105	109	3%
45	6	87	93	6%
55	11	44	55	20%
65	4	44	48	8%
75	2	40	42	4%
85	6	45	51	11%
IRON				
15	29	15	44	65%
25	59	42	101	59%
35	27	52	79	34%
45	31	34	65	47%
55	44	14	58	76%
65	29	19	48	60%
75	37	17	53	69%
85	26	29	53	48%
COPPER				
15	12	3	15	78%
25	11	12	22	48%
35	6	10	16	39%
45	13	8	20	62%
55	15	6	21	72%
65	4	11	16	29%
75	10	0.5	10	95%
85	8	4	13	67%
ZINC				
15	12	13	25	47%
25	19	n.d.	19	100%
35	8	10	18	43%
45	16	18	35	47%
55	13	13	26	51%
65	22	23	45	48%
75	166	23	189	88%
85	16	28	44	36%

Table 8 IV

Dissolved trace metals in the anoxic core F1 in ppb

Depth (cms)	HMW fraction(1)	LMW fraction(2)	Total calc.(3)	Total meas.(5)	% Bound (4)	% Bound (6)
MANGANESE						
5	197	1880	2077	1768	10%	0%
15	58	1450	1508	1780	4%	19%
25	47	608	655	851	7%	29%
35	3	83	86	90	4%	8%
45	11	5	16	42	70%*	88%*
55	7	7	14	39	50%*	82%*
65	1	40	41	39	2%	0%
75	1	17	18	13	7%	0%
IRON						
5	513	13	526	60	98%	78%
15	116	17	133	96	87%	82%
25	55	20	75	70	74%	71%
35	52	20	72	96	72%	79%
45	69	16	75	101	92%	84%
55	86	27	113	104	76%	74%
65	36	22	58	78	61%	72%
75	76	29	105	65	72%	55%
COPPER						
5	9	8	17	1	53%	0%
15	3	7	10	1	30%	0%
25	3	1	4	2	70%	40%
35	2	1	3	7	59%	81%
45	4	4	8	10	51%	60%
55	6	3	9	3	68%	10%
65	7	2	9	12	78%	83%
75	5	8	13	10	38%	25%
ZINC						
5	10	52	62	43	16%	0%
15	14	32	46	(13)	30%	0%
25	5	14	19	20	26%	43%
35	8	19	27	28	30%	47%
45	3	15	18	23	14%	35%
55	4	5	9	21	47%	76%
65	2	9	11	55	15%	84%
75	2	13	15	29	14%	55%

* Anomalous readings due to low Ultrafiltrate reading, removed before calculating the averages.

Table 8 V

Dissolved trace metals in the oxic core A4 in ppb

Depth (cms)	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
5	10	46	56	18%
15	13	56	69	19%
25	18	52	70	26%
35	5	81	86	6%
45	29	47	76	39%
55	1	53	54	2%
65	10	41	51	20%
IRON				
5	45	15	60	75%
15	32	15	47	67%
25	37	25	62	60%
35	69	26	95	72%
45	32	26	58	55%
55	5	7	12	44%
65	7	7	14	50%
COPPER				
5	2	24	26	6%
15	2	7	9	23%
25	0.5	7	7.5	7%
35	n.d.	5	5	10%
45	n.d.	5	5	10%
55	n.d.	3	3	15%
65	n.d.	3	3	15%
ZINC				
5	4	63	67	6%
15	15	41	56	26%
25	9	41	50	19%
35	16	27	43	37%
45	7	27	34	21%
55	4	20	24	17%
65	8	20	28	29%

Table 8 VI

Dissolved trace metals in the oxic core F4 in ppb

Depth (cms)	HMW fraction(1)	LMW fraction(2)	Total calc.(3)	Total meas.(5)	% Bound (4)	% Bound (6)
MANGANESE						
5	0	203	203		0%	
15	0	81	81	87	0%	7%
25	8	38	46	63	17%	40%
35	1	44	45		3%	
IRON						
5	10	21	31		31%	
15	6	7	13	50	46%	86%
25	30	6	36		83%	
35	12	23	35		33%	
COPPER						
5	0.3	5	5.3		6%	
15	0.1	6	6.1	1	2%	-ve
25	5	6	11	0	45%	-ve
35	0.9	6	6.9		13%	
ZINC						
5	0	31	31		0%	
15	0	31	31	13	0%	-ve
25	13	50	63	43	21%	-ve
35	5	14	19		27%	

SEA WATER F1/5						
Mn	4	35	39		10%	
Fe	1	6	7		14%	
Cu	4	12	16		25%	
Zn	4	3	7		57%	

Table 8 IX

Dissolved trace metals in the irradiated anoxic core A2 in ppb

Depth (cms)	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
5	135	9040	9175	1.5%
15	11	900	911	1%
25	1	150	151	1%
35	2	76	78	3%
45	6	50	56	11%
55	0	50	50	0%
65	3	55	58	6%
75	6	32	38	16%
85	4	50	54	8%
IRON				
5	18	80	98	18%
15	30	80	110	27%
25	24	41	65	37%
35	30	77	107	28%
45	28	125	153	18%
55	11	59	70	16%
65	23	73	96	24%
75	73	80	153	48%
85	37	111	148	25%
COPPER				
5	-ve	52	52	0%
15	1	17	18	6%
25	1	17	18	6%
35	0	17	17	0%
45	1	4	5	20%
55	1	20	21	5%
65	2	20	22	9%
75	3	12	15	20%
85	1	29	30	3%
ZINC				
5	-ve	600	600	0%
15	29	126	155	19%
25	23	105	128	18%
35	26	70	96	27%
45	28	50	78	36%
55	12	48	60	20%
65	7	110	117	6%
75	17	72	89	19%
85	14	133	147	10%

Table 8 X

Dissolved trace metals in the irradiated anoxic core A7 in ppb

Depth cms	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
5	42	1600	1642	3%
15	22	900	922	2%
25	7	310	317	2%
35	6	120	126	5%
45	2	87	89	2%
55	0	57	57	0%
65	0	60	60	0%
75	0	60	60	0%
85	4	40	44	9%
IRON				
5	196	275	471	42%
15	147	114	261	56%
25	75	116	191	39%
35	98	170	268	37%
45	66	55	121	55%
55	99	101	200	50%
65	63	73	136	46%
75	50	82	132	38%
85	56	125	181	31%
COPPER				
5	2	20	22	11%
15	3	12	15	20%
25	1	17	18	6%
35	5	21	26	20%
45	1	17	18	6%
55	2	13	15	13%
65	3	14	17	18%
75	1	17	18	6%
85	2	84	86	2%
ZINC				
5	88	449	537	16%
15	47	109	156	30%
25	32	121	153	21%
35	93	121	214	43%
45	12	35	47	26%
55	21	110	131	16%
65	22	110	132	17%
75	30	47	77	39%
85	17	49	66	26%

Table 8 XI

Dissolved trace metals in the irradiated oxic core A4 in ppb

Depth (cms)	HMW fraction (1)	LMW fraction (2)	Total calc. (3)	% Bound (4)
MANGANESE				
5	0	38	38	0%
15	0	53	53	0%
25	1	47	48	2%
35	2	85	87	2%
45	2	48	50	4%
55	2	42	44	5%
65	0	20	20	0%
75	0	15	15	0%
IRON				
5	37	111	148	25%
15	19	57	76	25%
25	14	75	89	16%
35	27	37	64	42%
45	60	49	109	55%
55	18	35	53	34%
65	13	49	62	21%
75	93	56	152	63%
COPPER				
5	0	22	22	0%
15	0	10	10	0%
25	1	10	11	10%
35	2	5	7	29%
45	0	9	9	0%
55	0	5	5	0%
65	0	9	9	0%
75	1	11	12	8%
ZINC				
5	10	133	143	7%
15	8	73	81	10%
25	12	53	65	18%
35	10	37	47	21%
45	11	34	45	24%
55	12	57	69	16%
65	23	72	95	24%
75	5	63	68	7%

totals obtained by these two independent methods are comparable within the limits of reasonable analytical error. In addition, the percentage of trace metal bound in the high molecular weight material was calculated by two independent methods (Table 8 IV) based on the totals measured directly and calculated. The average percentage bound for each element calculated by these two methods is Mn 9%, Fe 74%, Zn 43% and Cu 37% as calculated using the directly measured totals and the % bound calculated from the ultrafiltrate and retentate of Mn 6%, Fe 79%, Zn 24% and Cu 59%. The differences observed between these two analytical methods do not affect the qualitative conclusions drawn about the speciation of trace metals within pore waters.

The trace metal analyses for the pore waters extracted from five cores are given in Tables 8 II - VI. The profiles for each of the metals analysed with depth are given in Figures 8.4 - 7. Cores F1, A7 and A2 are reducing cores with the oxic - anoxic redox boundary being very close to the sediment/water interface. These cores show a dramatic surface enrichment of Mn, 727 - 13,500 ppb which decreases to a value of 39 - 56 ppb at a depth of 65 centimetres. A similar surface enrichment of Mn has been observed in the pore waters of Loch Fyne (Duchart et al., 1973) and of some Norwegian fjords (Taylor, 1974). This surface enrichment is not present in cores A4 or F4, which remain oxic throughout their length, nor has such an enrichment been observed in the cores from Saanich Inlet where the oxic - anoxic boundary was periodically in the water column (Presley et al., 1972). It was thus inferred that the surface enrichment of Mn is related to the oxic - anoxic redox boundary.

The profiles of Fe and Cu show no systematic trends with depth

in the anoxic sediments (Table 8 II - IV). The average values of these metals for the three reducing cores (F1, A2 and A7) are; Fe (61, 67 and 84 ppb) and Cu (19, 17 and 6 ppb). Zn appears to vary systematically with depth, cores F1 (62→15 ppb) and A2 (423 - 98 →27 ppb) show a decrease in concentration with depth, while core A7 (25→44 - 189 ppb) shows an increase in Zn from the surface to the bottom of the core. Core A3, another anoxic core shows no systematic trend with depth. However, all other aspects of the geochemistry of these anoxic cores appear to be similar, and thus no explanation for this behaviour is given.

The average concentrations of these three trace metals compare to those found in the anoxic cores of Loch Fyne, Fe 80 - 180 ppb, Zn 36 - 116 ppb and Cu 20 - 270 ppb (Duchart et al., 1973) and in the anoxic basins in the Santa Barbara basin, Fe 13 - 69 ppb, Zn 42 - 72 ppb and Cu 1.8 - 5.0 ppb (Brooks et al., 1968). The average concentrations of trace metals in the oxic cores of Loch Beg are also similar in magnitude to those found in the reducing cores of Loch Duich; Fe 27 and 50 ppb, Zn 36 and 43 ppb and Cu 7 and 8 ppb, and show no significant trend with depth. They are approximately an order of magnitude greater than the concentration of trace metals found in the overlying sea water; Fe 4.1 ppb, Zn 5.3 ppb and Cu 0.9 ppb.

A number of publications have reported analyses of sea water for certain trace metals before and after oxidation, the difference between these two values being used as a measure of the organically bound trace metals present (Barsdate and Matson, 1966; Alexander and Corcoran, 1967; Williams, 1969; Foster and Morris, 1971; Slowey and Hood, 1971 and Fitzgerald and Lyons, 1973). These publications

show that there is an increase in the measured concentration of trace metals in sea water after oxidation as compared to before. A similar experiment was performed on the pore waters from Loch Duich; the results are presented in Table 8 VIII. These values represent the average concentrations of the trace metal determinations for each core; the data from which these results were determined are presented in Tables 8 II, III, V and IX - XI.

There is a significant increase in the measured concentration of Fe (42 - 69%) and Zn (16 - 70%) after oxidation both for the two anoxic cores and for the oxic core. Mn and Cu do not show a significant increase after oxidation for the reducing core, although there is some increase in Cu for the oxic core (27%). These results show that there is a significant degree of organic chelation for Fe and Zn.

Kamps-Nielsen (1972) noted that this method of analysis will give only a minimum value for the trace metal - organic chelates. In simple calculations based on the competition for copper between DEDTC (the chelating agent) and the natural organic chelates already present, he shows that analysis of the untreated sea water measures not only the ionic metal, but also all the metal bound to organic chelates with a stability constant less than 10^{30}. It is thus possible that large proportions of the remaining trace metals which are analysed in the untreated sample and considered by other workers as unbound could still be chelated to organics.

Ultrafiltration of pore waters

This method was used to separate low molecular weight material (LMW) which passes through the UM-2 (nominal molecular weight retained = 1000) ultrafilter from the high molecular weight material

Table 8 VIII

The change in concentration of trace metals as a result of oxidation

Location and Sample	Element	Concentration of Element		Organic Bound %*	Reference
		Untreated	Oxidised		
Loch Duich Anoxic core A2	Fe	61	111	45%	
	Zn	91	108	16%	
	Cu	19	18	-6%	
	Mn	-	-	-5%	
Loch Duich Anoxic core A7	Fe	67	218	69%	
	Zn	50	168	70%	
	Cu	17	18	6%	
	Mn	-	-	13%	
Loch Duich Oxic core A4	Fe	50	86	42%	
	Zn	43	77	46%	
	Cu	8	11	27%	
	Mn	-	-	-	
Menai straits	Cu			9-40%	Foster and Morris, 1971
Long Island Sound	Hg			45-75%	Fitzgerald and Lyons, 1973
California Basins.	Cu			5-28%	Williams, 1969b

* Organic Bound % = $\frac{\text{Untreated}}{\text{Oxidised}} \times 100\%$

(HMW), which is retained behind the filter (Gjessing, 1970; Willander, 1972; Schindler et al., 1972; Fitzgerald and Lyons, 1973). The results for the analysis of the trace metals in the ultrafiltrate and retentate are presented in Tables 8 II - VI.

Figures 8.4 - 7 represent graphically the concentration of trace metals (Mn, Fe, Cu and Zn) present in the HMW and LMW fractions. Figure 8.8 shows the percentage of the total trace metal which is present in the HMW fraction in the five cores analysed; A7, A2 and F1 represent reducing conditions, while A4 and F4 are oxic.

Mn behaves in a significantly different manner from Fe, Cu and Zn within all the cores analysed. The surface enrichment of Mn which was noted in the pore waters of the reducing cores is present almost entirely in the LMW fraction. The fraction of Mn present in the HMW fraction of anoxic cores (5 - 12%) is always very much lower than the HMW fraction of Fe (56 - 77%), Zn (27 - 58%) and Cu (61 - 66%).

There are no trends in the total dissolved Fe and Cu (Figures 8.5 and 8.6), nor are there any simple trends in the HMW or LMW fractions for any of the cores. In those cores F1, A2 and A7 in which a trend in concentration of Zn with depth is observed, the changes, whether increasing or decreasing, are present mainly in the LMW fraction (Figure 5.7). However, for all of these trace metals the LMW fraction does not show any simple inverse relationship to the concentration of sulphide in the pore waters as would be expected if the solubility of the trace metals was controlled by the precipitation of trace metal ions as sulphides. Similarly, although it has been shown in Chapter 6 that there is a simple accumulation of HMW organics

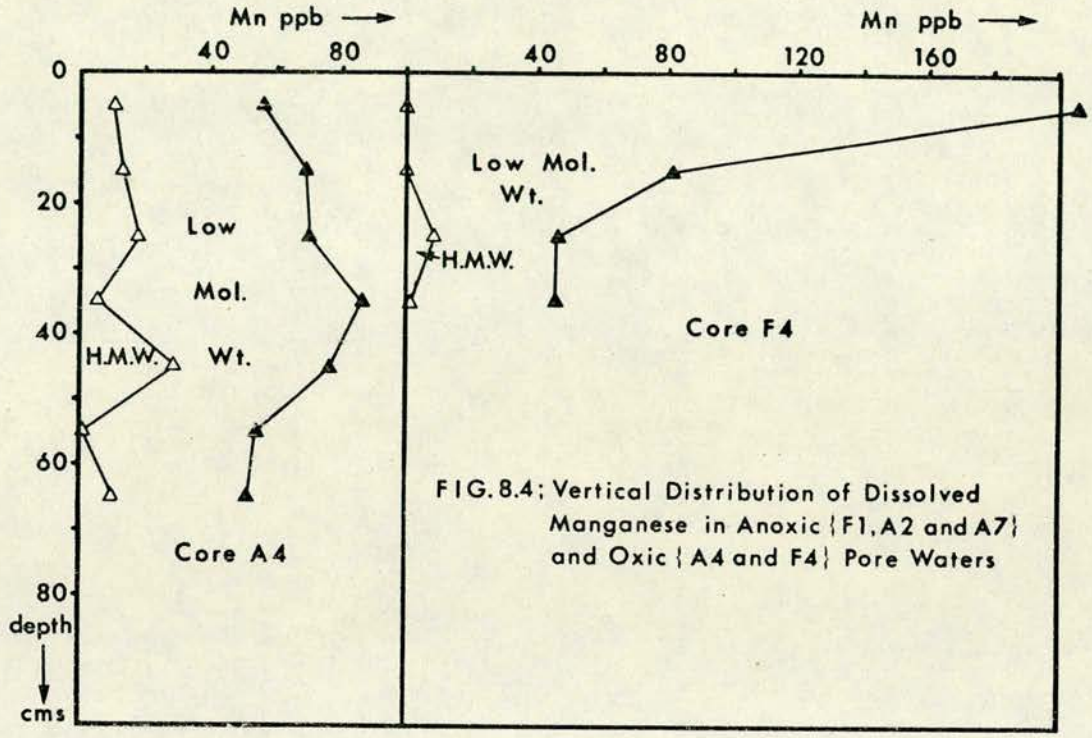
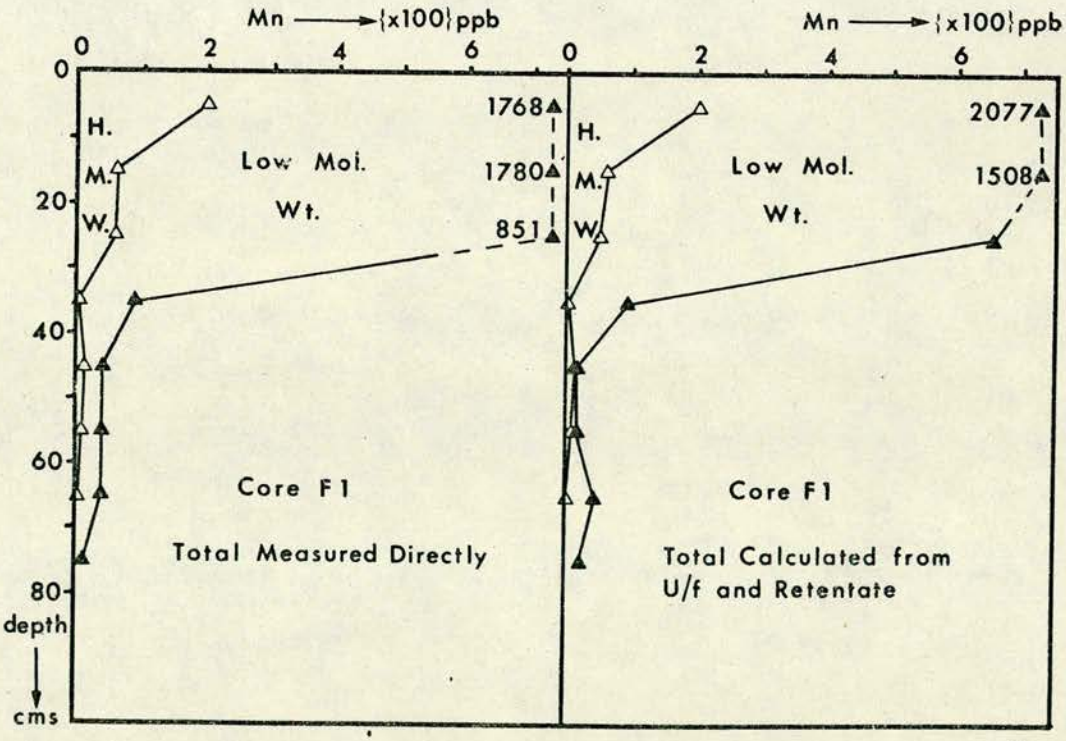


FIG. 8.4; Vertical Distribution of Dissolved Manganese in Anoxic {F1, A2 and A7} and Oxic {A4 and F4} Pore Waters



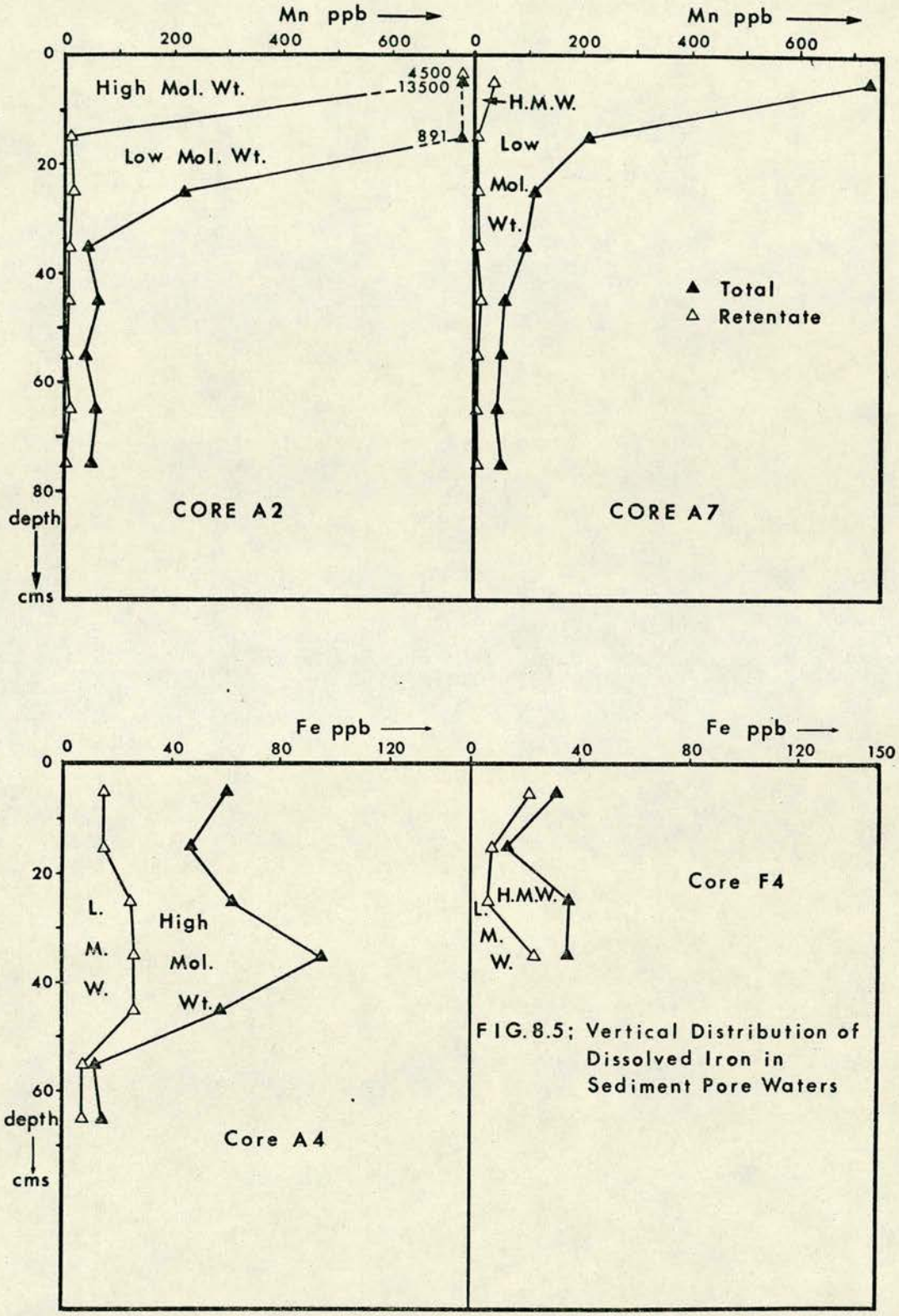
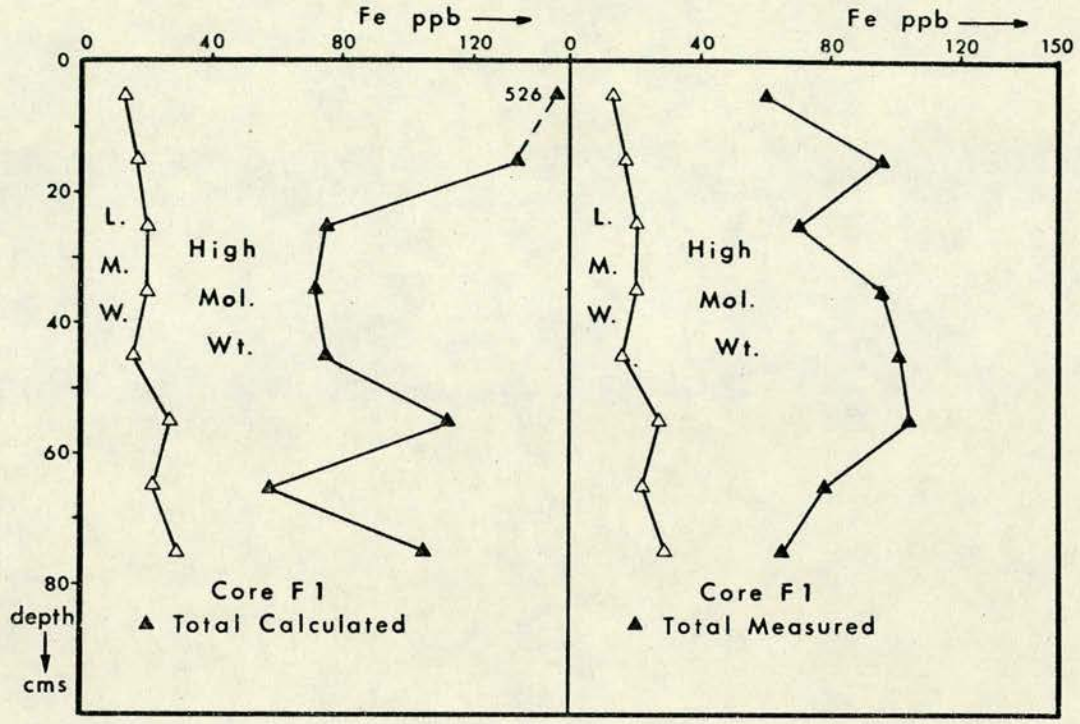
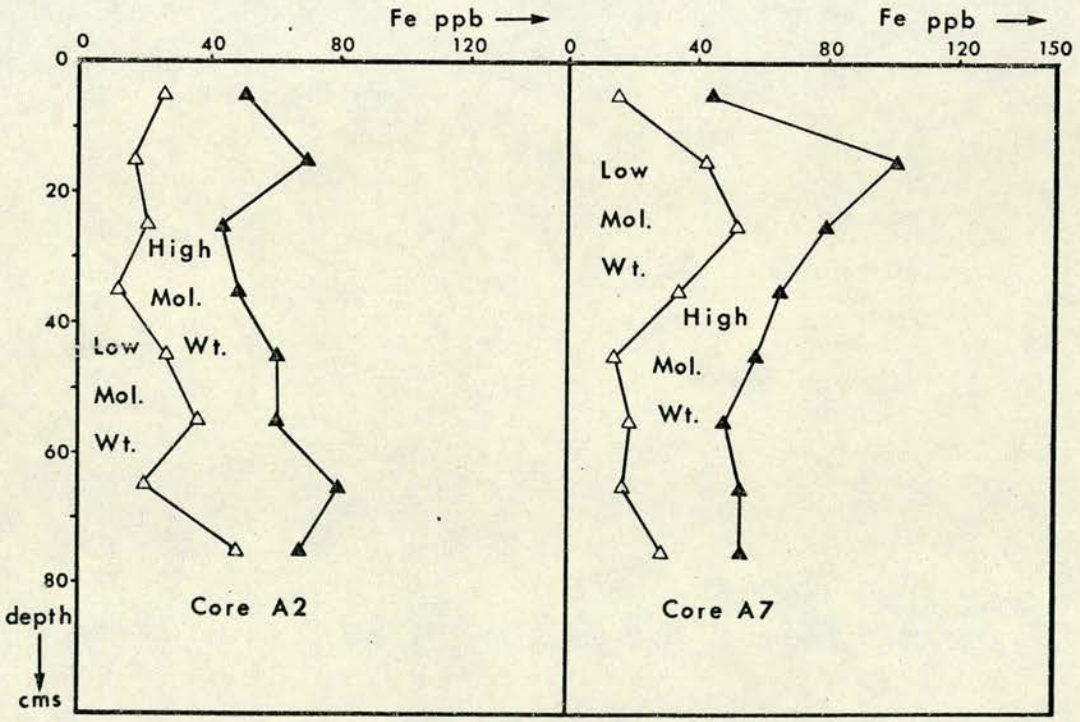


FIG. 8.5; Vertical Distribution of Dissolved Iron in Sediment Pore Waters


Fe ppb
0
40
80
120
150
526
L.
M.
W.
High
Mol.
Wt.
Core F1
▲ Total Calculated
Core F1
▲ Total Measured
depth
cms


Fe ppb
0
40
80
120
150
High
Mol.
Wt.
Low
Mol.
Wt.
Core A2
Core A7
depth
cms

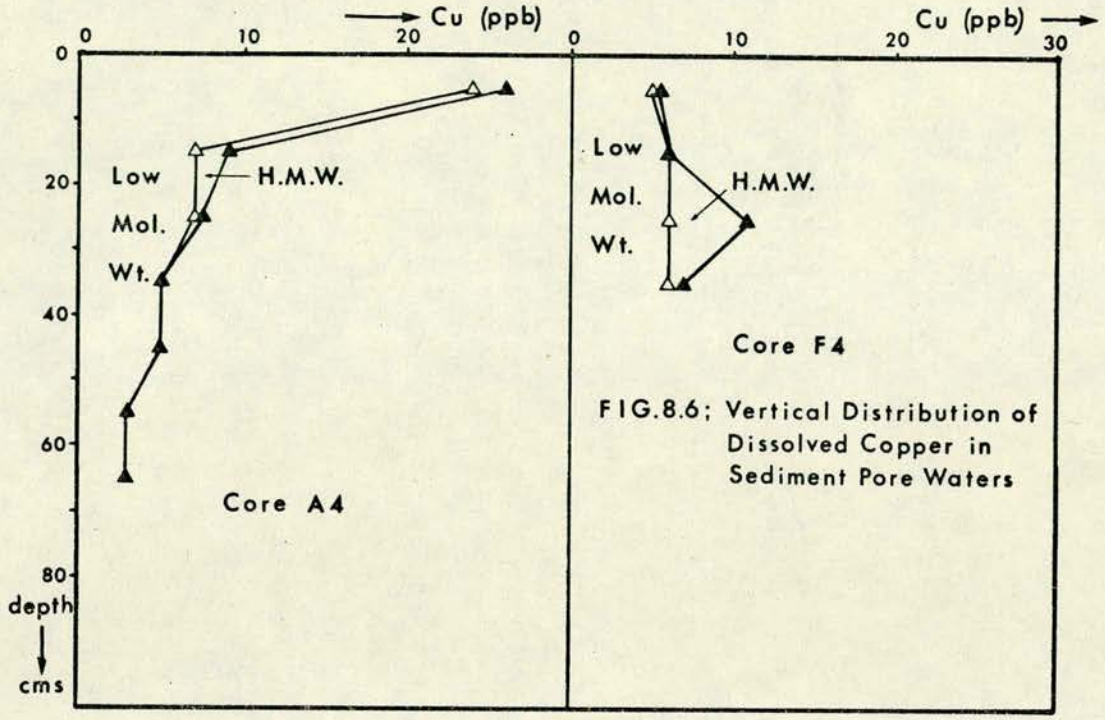
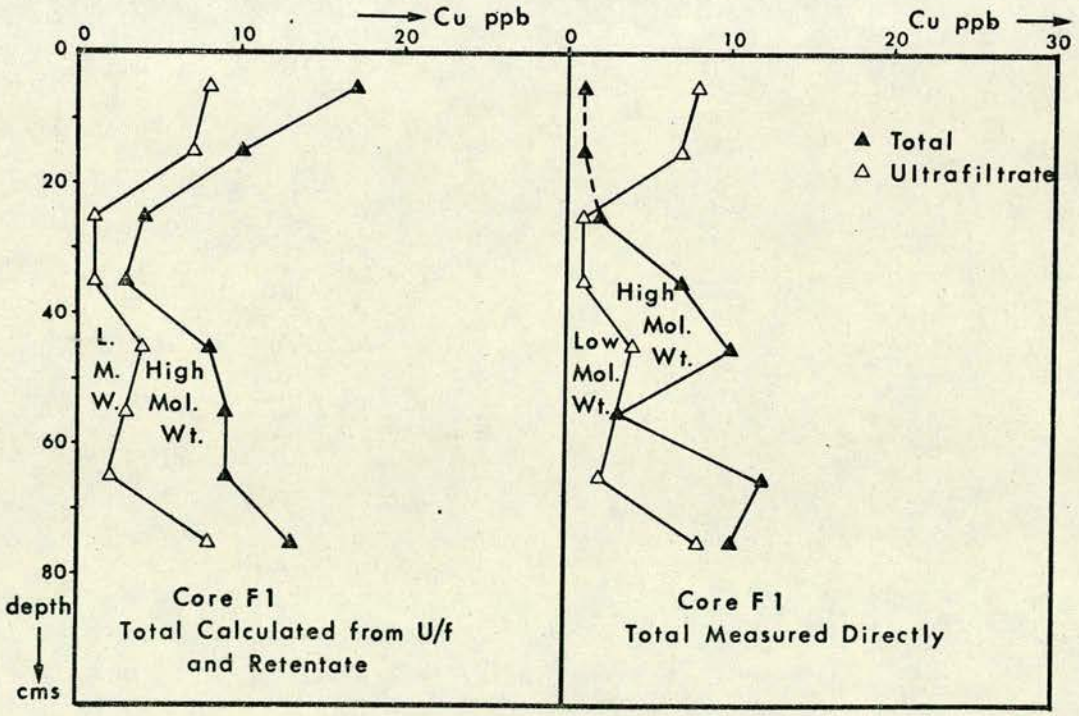
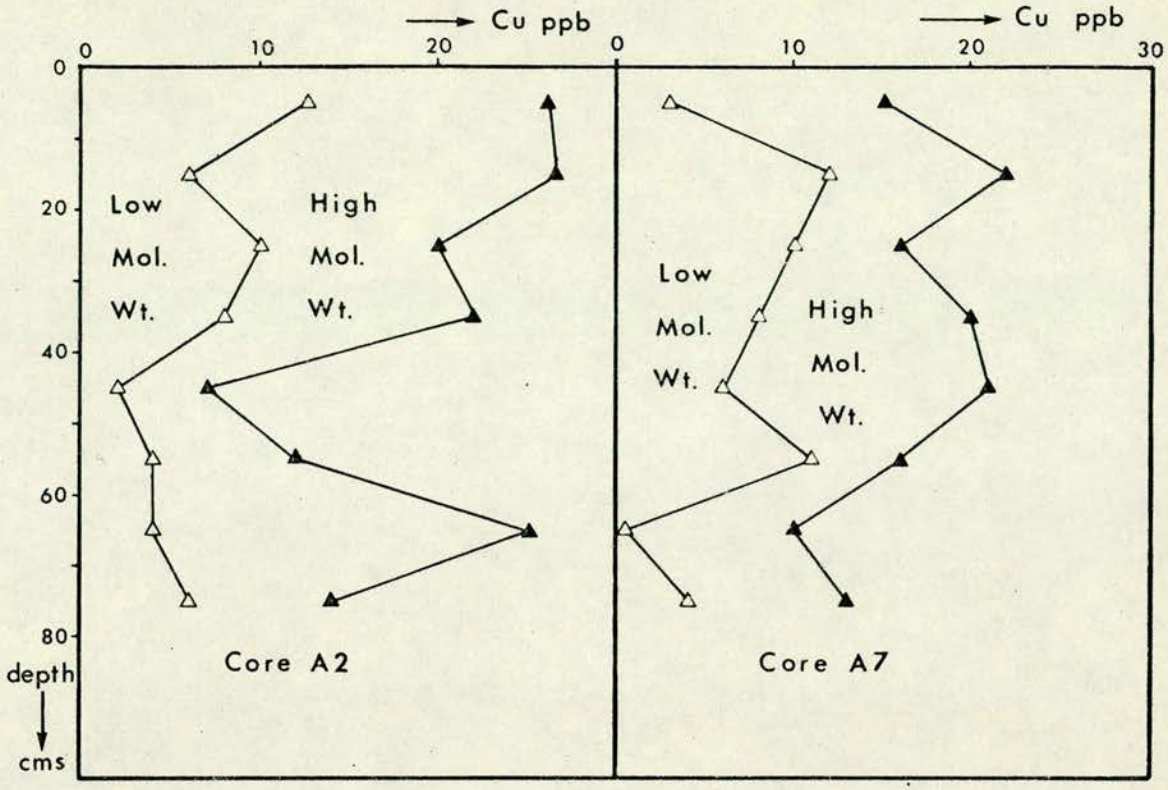


FIG.8.6; Vertical Distribution of Dissolved Copper in Sediment Pore Waters





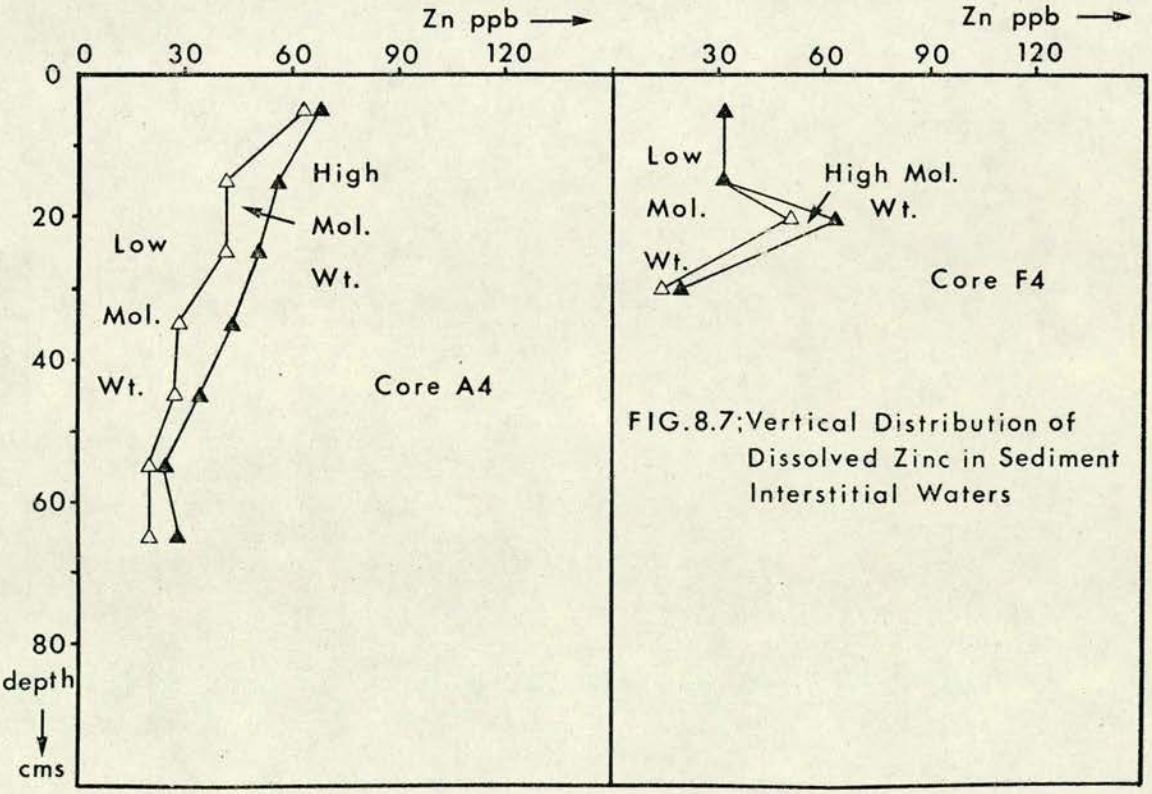
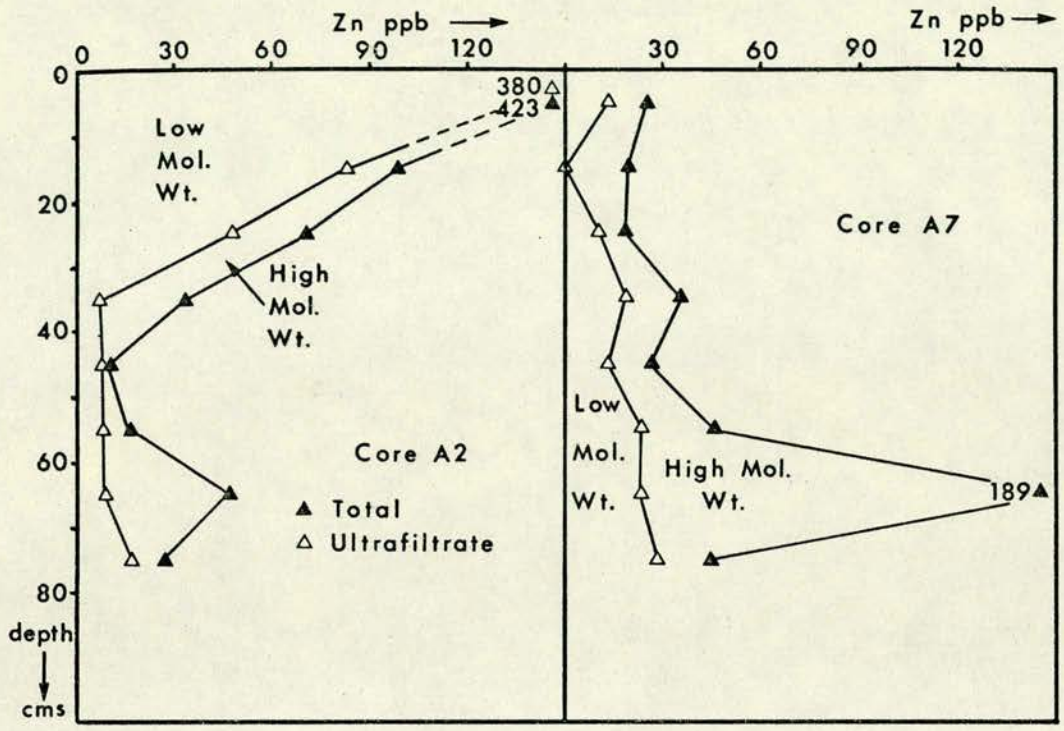
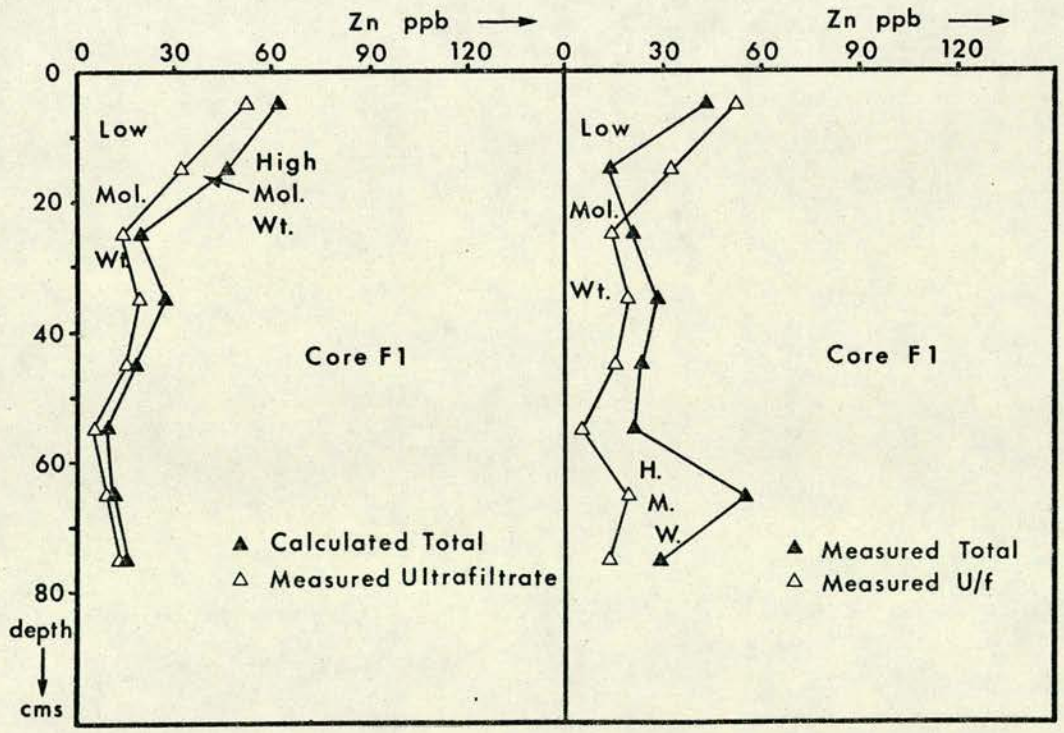


FIG. 8.7; Vertical Distribution of Dissolved Zinc in Sediment Interstitial Waters


Zn ppb
0
30
60
90
120
380
423
Low
Mol.
Wt.
High
Mol.
Wt.
Core A2
Total
Ultrafiltrate
Core A7
Low
Mol.
Wt.
High Mol.
Wt.
189
depth
cms


Zn ppb
0
30
60
90
120
Low
Mol.
Wt.
High
Mol.
Wt.
Core F1
Calculated Total
Measured Ultrafiltrate
H.
M.
W.
Measured Total
Measured U/f
depth
cms

in anoxic pore waters, there is no parallel increase in the concentration of Fe, Cu and Zn in the HMW fraction. Thus there is no simple correlation between trace metals and total DOC.

In the oxic cores, although the fraction of Mn bound in the HMW phase (5 - 19%) is the lowest of the four elements analysed, the fraction of Zn (12 - 22%) and Cu ($<$12 - 17%) bound in the HMW fraction is significantly lower than that found in anoxic cores and almost as low as Mn. 48 - 60% of the Fe analysed in the oxic core is present in the HMW fraction.

The LMW fraction could contain not only labile inorganic complexes[1], but also metal bound to inorganic complexes such as polysulphides and oxide-hydroxides and low molecular weight organic matter such as amino acids and porphyrins. Similarly, although it is known that the HMW fraction contains a high concentration of "humic" substances, it is also possible that it contains a proportion of inorganic particles which passed through the 0.45μ Sartorius filter, but which were retained behind the ultrafilter.

In order to differentiate between the organic and inorganic phases of the HMW fraction, an experiment was performed in which the pore waters were oxidised by UV light in a stream of oxygen until all the organic matter was destroyed; the sample was then ultrafiltered and analysed.

The results for the analysis of trace metals after oxidation

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[1] Mn, Fe, Cu and Zn tend to form ion pairs and labile inorganic complexes with Cl, SO_4^{2-}, HCO_3^-, etc. when "free ions" become dissolved in sea water (Goldberg, 1965).

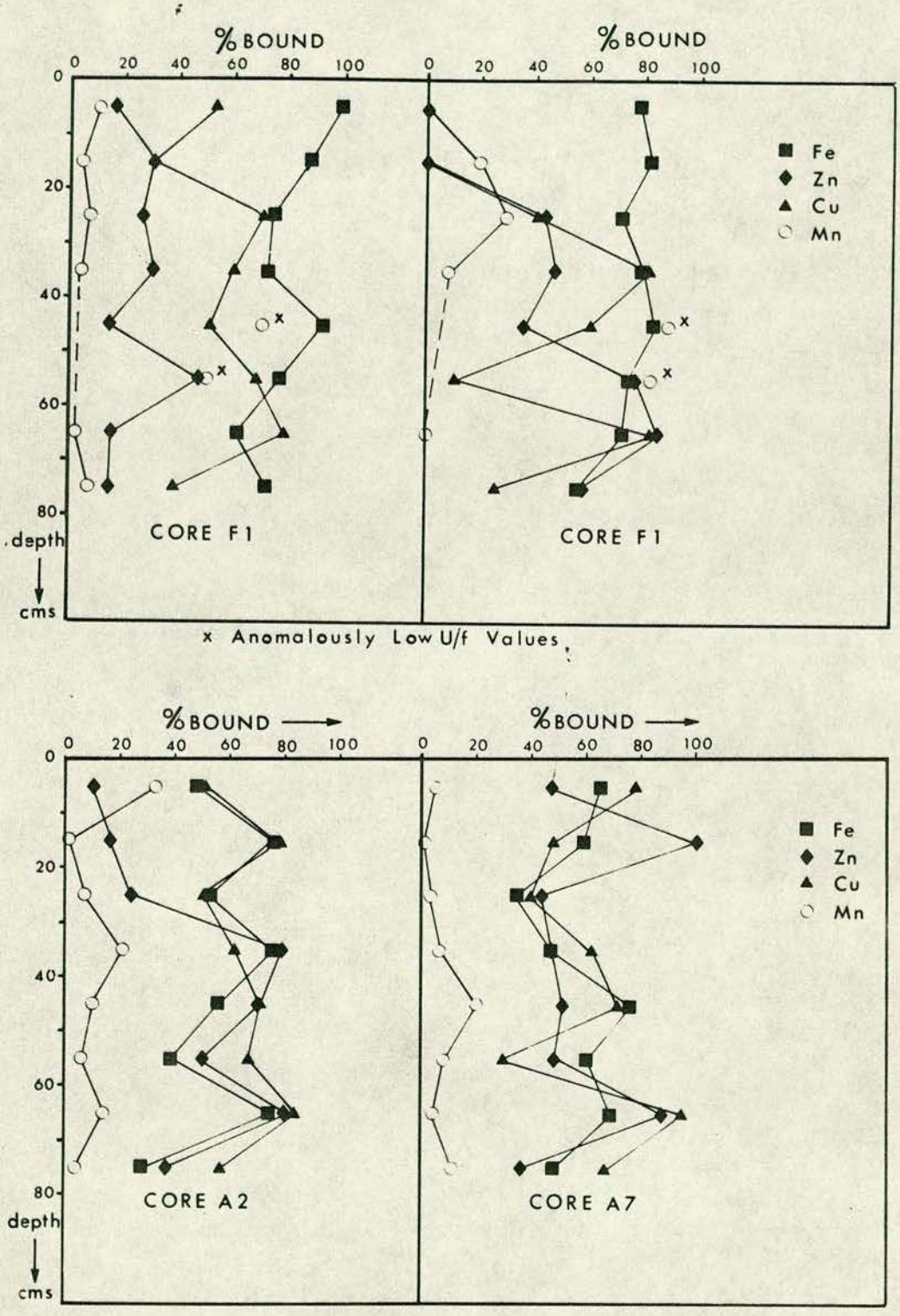


FIG. 8.8; Vertical Distribution of % Metal Bound in HMW Fraction of Untreated Pore Waters

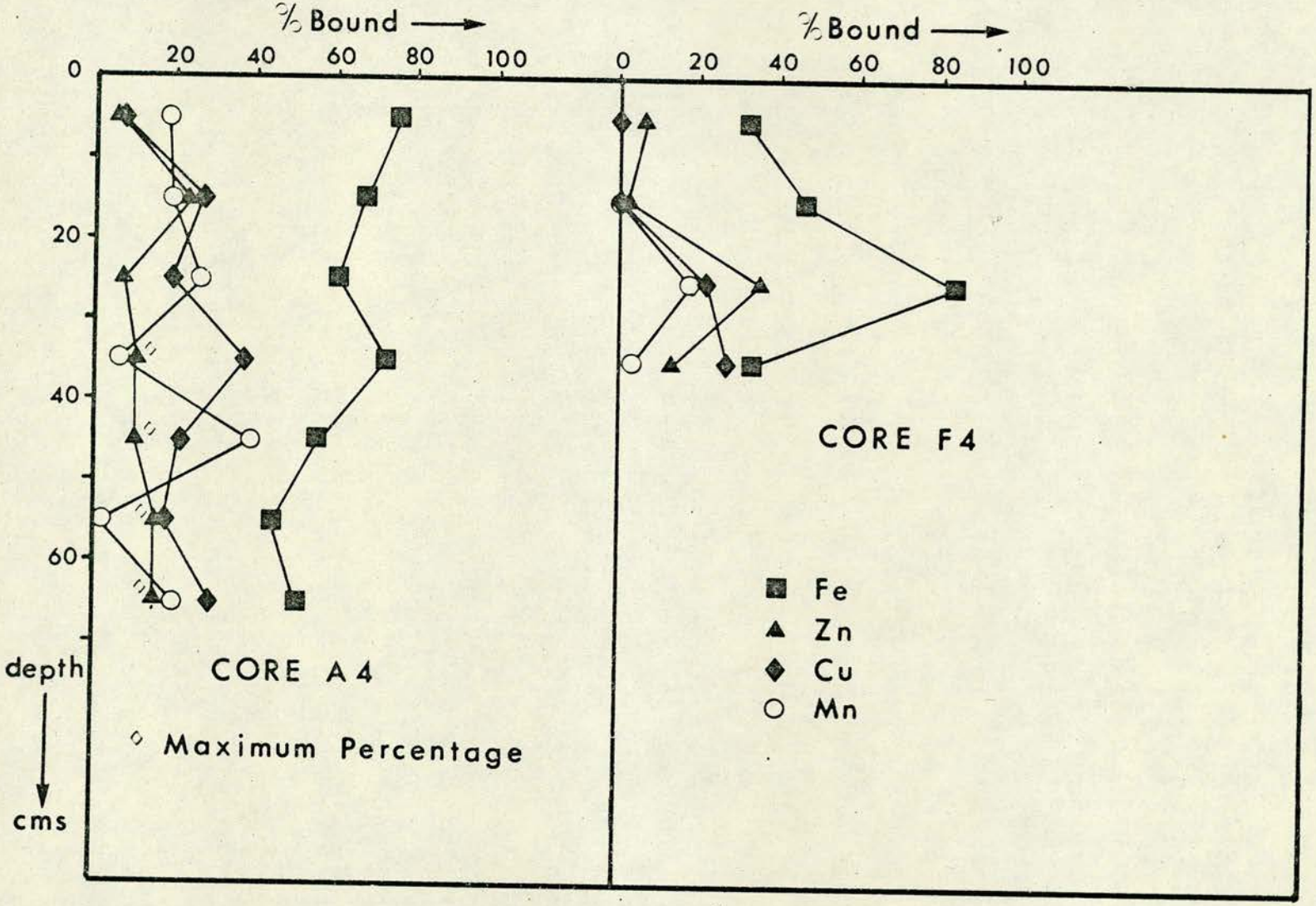
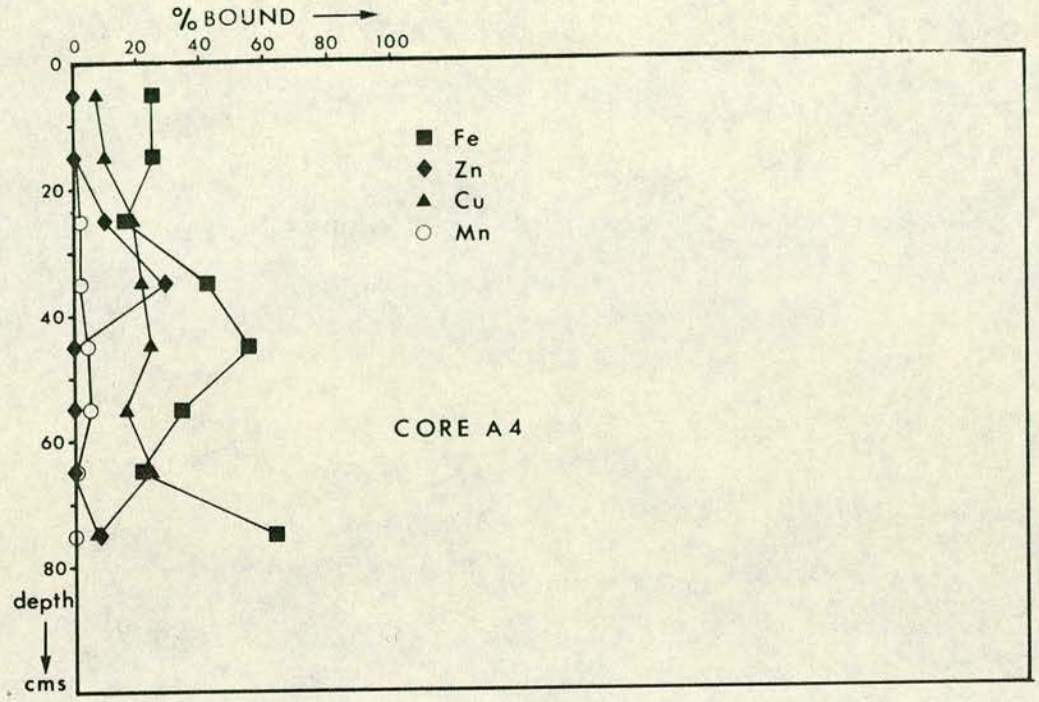


FIG.8.8; Continued



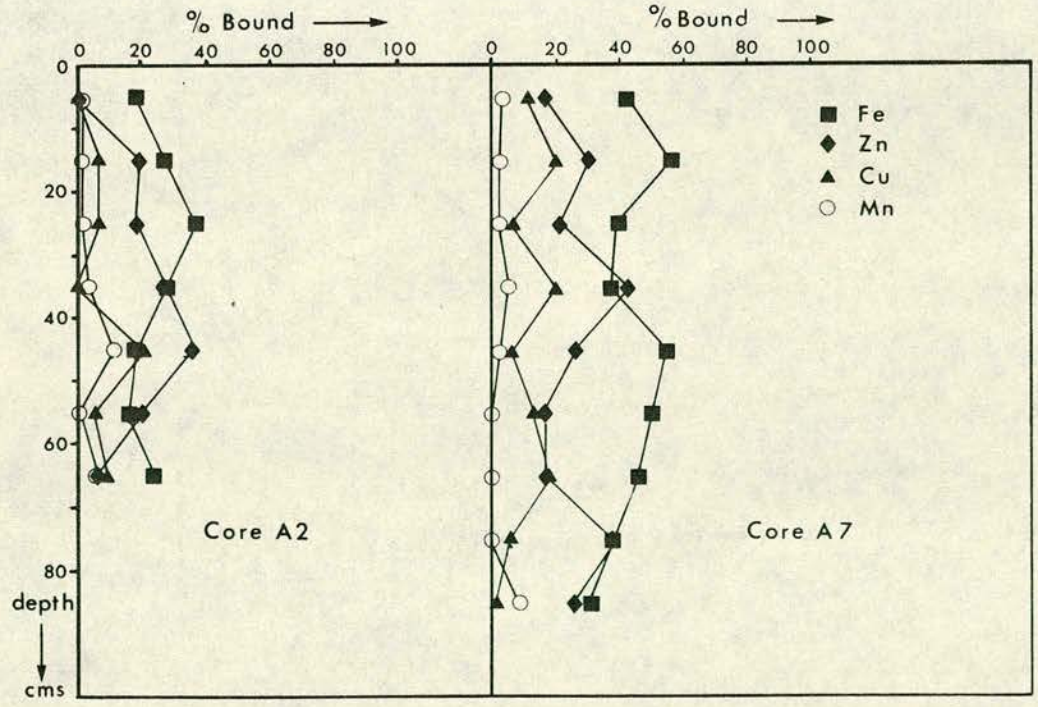


FIG.8.9; Vertical Distribution of % Metal Bound in HMW Fraction of Oxidised Pore Waters

are presented in Tables 8 IX - XI. Figure 8.9 shows the percentage bound in the HMW fraction after oxidation. These results show that there is a significant reduction in the percentage bound in the HMW fraction for all the elements considered; Mn from an average of 5 - 19% to 2 - 3%, Fe from 48 - 77% to 24 - 44%, Zn from 12 - 58% to 11 - 18% and Cu from 17 - 66% to 6 - 26%. All these reductions could be due to the destruction of organic chelates by oxidation and the subsequent release of trace metals. However, it is also possible to interpret some or all of this reduction in the proportion of bound trace metals as being due to the breakdown of HMW inorganic colloids such as iron oxide-hydroxides or polysulphides to form LMW material due to the action of hydrogen ions since the pore waters were acidified to pH = 2 with hydrochloric acid prior to oxidation. The presence of a significant quantity of Fe in the HMW material after oxidation could be due to inorganic particles resistant to UV oxidation and stable in acid solution from the original pore waters or produced during oxidation.

Trace metals bound in the acid insoluble humic acid precipitate

The humic acid precipitate was analysed quantitatively for Fe while scans were performed to search for the presence of Zn, Cu and Pb. However, none of these latter three elements were detected by the X-ray fluorescence method used.

The Fe concentration varied from 0.01% to 1.35% of the total humic acid with an average content of 0.35% (Table 6 V). This represents a concentration of 8 - 20 ppb of Fe bound to humic acid in the original pore waters. This is a minimum value for the concentration of Fe chelated to humic acids in the untreated pore waters

since acidification will tend to strip metals from chelates, particularly where the binding is through hydroxyl or carboxyl groups.

8.4 Discussion of results

Speciation of trace metals in pore waters: Mn

Mn is the only dissolved trace metal analysed which shows a recognisable diagenetic trend, a surface enrichment of the metal in the anoxic cores. This enrichment is related to the oxic - anoxic boundary, no surface enrichment occurring in the oxic cores. In addition, a high proportion of the metal is present in the LMW fraction, and there is no significant increase in the concentration of Mn analysed after oxidation. All these observations are consistent with the conclusion that Mn is present in the pore waters as labile inorganic complexes and that the concentration profile observed can best be interpreted by a diffusion model similar to that evoked to explain the Mn distribution in sediments from the Arctic basin (Li et al., 1969) and Loch Fyne (Calvert and Price, 1972).

Figure 8.10 represents diagrammatically the processes within the sediment which are thought to be important in controlling the solubility of Mn in such pore waters. It is assumed in this model of the observed Mn profile that the pore waters are in a steady state condition. Mn is sedimented mainly as Mn(IV) phases, the form which is thermodynamically stable at the pE and pH conditions present in the water column and at the sediment - water interface (Stumm and Morgan, 1970). After burial, the pE drops as a result of the metabolic decomposition of organic matter and a fraction of this Mn(IV) is solubilised into the pore waters as Mn(II). This dissolution of

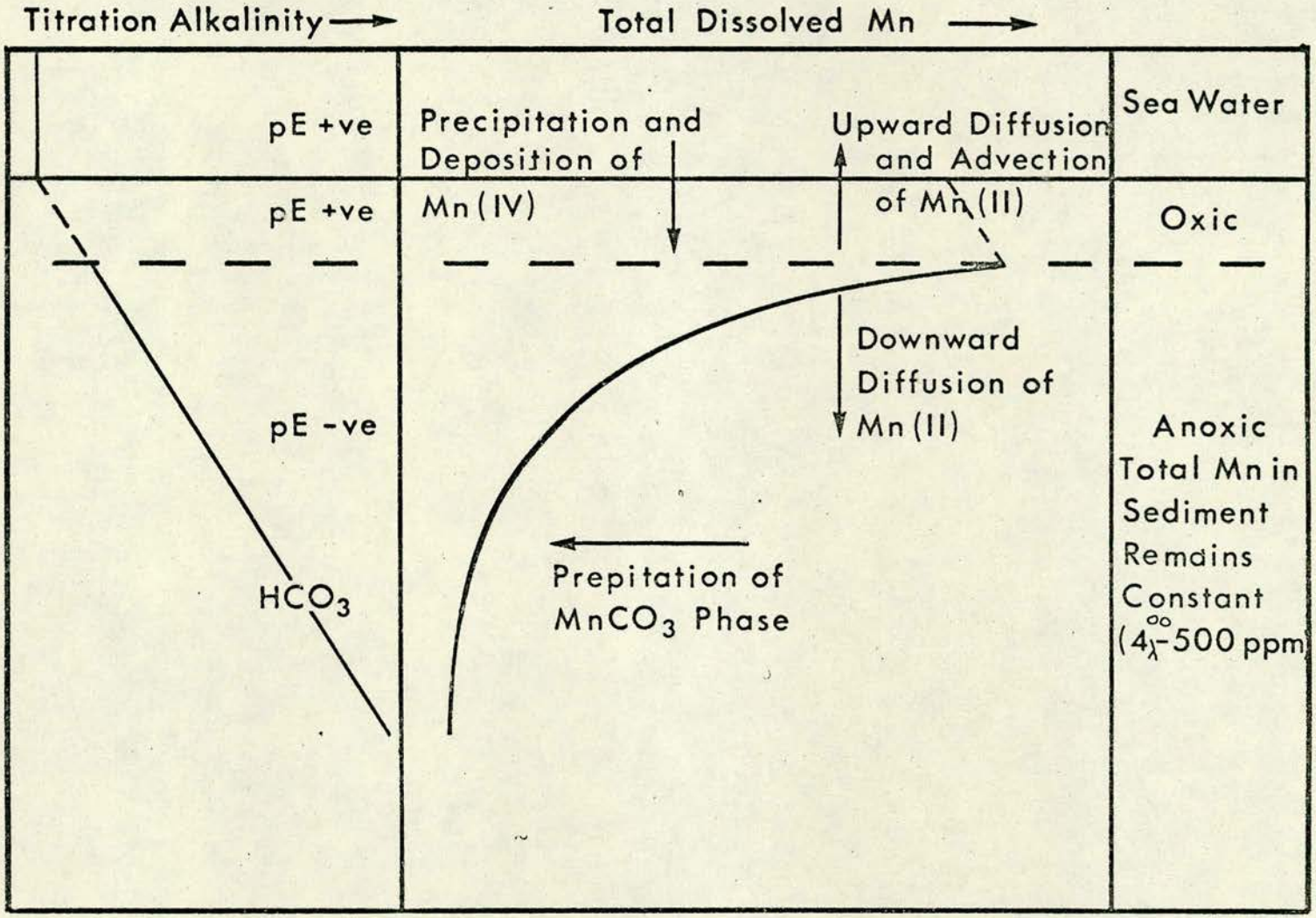


FIG 8.10; Processes of Diffusion and Precipitation Involving Dissolved Manganese in the Pore Waters of Recent Sediments.

Mn causes a diffusion gradient to be set up, both upwards and downwards.

The diffusion of Mn upwards creates a recycling process; the Mn(II) diffuses back across the oxic - anoxic redox boundary, where it is reprecipitated as Mn(IV). This Mn(IV) precipitate can be resuspended as particulate matter in the water column or it can remain within the sediment, forming a brown oxic layer. Such a surface layer has been observed in sediments from Loch Fyne (Calvert and Price, 1972) and in the Arctic basin (Li et al., 1969). In the latter study area the oxic layer was so thick (70 cms) that the pore waters within it could be sampled; they showed a diffusion profile consistent with this model of upward diffusing Mn(II). In Loch Duich the brown oxic layer was only recovered once and found to be a few millimetres thick. It is suggested that this layer is present in all the cores, but that generally it is lost due to the splash effect of the gravity corer.

In order to explain the observed enrichment of dissolved Mn very close to the sediment - water interface, a mechanism must be postulated that can maintain the maximum directly below the sediment surface and prevent it from migrating downwards as a result of diffusion and further sedimentation. Two possible mechanisms are considered: the upward advection of interstitial waters relative to a given sediment horizon resulting from the compaction of the sediment (Taylor, 1974), and the removal of Mn(II) at depth as a result of precipitation as a manganous carbonate phase (Calvert and Price, 1972; Li et al., 1969).

a) Advection - Diffusion model

As a sediment is buried, compaction occurs, resulting in the upward advection of pore waters. Taylor (1974) explains the maintenance of the high surface enrichment of pore water Mn in the surface layers of sediment from a Norwegian fjord as being due to the upward migration of pore waters balancing the downward diffusion of Mn(II).

In order to estimate the relative importance of advection and diffusion, it is necessary to know the rate of sedimentation, the change of porosity with depth and the diffusion rate of Mn(II) ions in sediment interstitial waters. A discussion on estimates of the sedimentation rate for the sediments of the Loch Duich basin is presented in Chapter 3.8. The estimate for this term (0.1 - 0.01 cms/yr) that is available for these sediments is reliable only to one order of magnitude. Estimates of the value for the diffusion constant of Mn(D) in pore waters are even less precise, varying from D equal to 10^{-9} - 10^{-10} cms^2/sec (Duursma and Bosch, 1970) to D of 2×10^{-5}, the value used by Lynn and Bonatti (1965). Tzur (1971) shows that if one uses Duursma's smaller values for D, then advection becomes significant for a sediment which is accumulating at a rate greater than 3×10^{-4} cms/yr, which is a slow sedimentation rate for a shallow coastal marine sediment. In Loch Duich a sedimentation rate of 10^{-1} to 10^{-2} cms/yr is considered to be a reasonable estimate, while most workers use a diffusion coefficient of 10^{-6} cm^2/sec. Using such values, advection is found to be insignificant (Tzur, 1971). However, it is possible by choosing other not unreasonable values for these two terms, to suggest that advection is the major

process controlling the distribution of dissolved Mn in pore waters.

b) Precipitation of Mn within the core

It is possible to maintain a profile of Mn such as that observed in the pore waters by supplying Mn(II) to the pore waters close to the surface and removing it at depth into a solid sediment phase. Robbins and Callender (1975) assume that the distribution of Mn in Lake Michigan sediments is controlled by the precipitation of a carbonate phase. Calvert and Price (1972) demonstrate the presence of such a manganous carbonate phase both as concretions and in the matrix of recent sediments from Loch Fyne. However, it is difficult to compare directly the processes which control Mn distribution in the sediments of these two lochs, because Loch Fyne has a significantly higher concentration of Mn both in the sediment (0.06 - 5.17%) and in the pore waters (0.26 - 13.47 ppm) compared to (0.04%) and (0.04 - 10 ppm) in the sediments of Loch Duich. In particular it is possible to observe directly a manganous carbonate phase in the sediments of Loch Fyne by X-ray diffraction and by chemical analysis. If such a phase were present in the sediment of Loch Duich, it would not be possible to detect it by X-ray diffraction because the total concentration of disseminated manganous carbonate within the sediment would be too low. It is also not possible to observe this precipitation by examining the bulk changes in solid Mn in the sediment, since the total change in the concentration of all the dissolved Mn would result in a change of less than 0.5% in the total measured Mn (4 - 500 ppm) in the sediment.

A theoretical calculation was performed to estimate the degree of saturation of Loch Duich pore waters (S) with respect to manganous

carbonate using the data obtained in this study for the concentration of dissolved Mn, titration alkalinity and a reasonable range of values for the pH of anoxic pore waters.

$$S = \frac{[Mn(II)][CO_3^{2-}]}{K_{sp}} \qquad \text{—— Equation (1)}$$

Where S = 1 for a saturated solution.

In order to solve this equation, it is necessary to obtain estimates of Mn(II), CO_3 and K_{sp}.

$K_{sp} = 2 \times 10^{-10}$ to 5×10^{-11} (Li et al., 1969)

Mn(II) has been measured in the pore waters of Loch Duich as an equilibrium value of approximately 55 ppb = 1.1×10^{-6} mMoles/ltr.

Carbonate concentration can be estimated from the alkalinity and pH of the interstitial waters using equation (2):

$$CO_3^{2-} = C.A./(2 + a_H/K'_2) \qquad \text{—— Equation (2)}$$

(Edmond and Gieskes, 1970)

where K'_2 is the second apparent dissociation constant of the carbonate-bicarbonate equation and equals 5×10^{-10}.

C.A. is the carbonate alkalinity which is approximately equal to the titration alkalinity, which is measured as 50 meq/ltr

and

a_H is the hydrogen ion activity which approximates to pH.

The equation is very sensitive to changes in pH. Two values of pH, 8.0 and 7.0 were chosen, resulting in a maximum and minimum value of carbonate ions and thus S.

Solving equation (2)

CO_3^{2-} = 1.1×10^{-3} moles/ltr for pH = 8

and = 1.2×10^{-4} moles/ltr for pH = 7

Substituting values into equation (1)

For pH = 8:

S = 5.5 for $K_{sp} = 2 \times 10^{-10}$

S = 22 for $K_{sp} = 5 \times 10^{-11}$

and for pH = 7:

S = 0.6 for $K_{sp} = 2 \times 10^{-10}$

S = 2.4 for $K_{sp} = 5 \times 10^{-11}$

Thus it is shown that the solution to this equation is highly sensitive to small changes in pH. However, for the values of Mn(II), alkalinity and pH chosen, the pore waters are either close to saturation or supersaturated with respect to manganous carbonate. It is thus concluded that the depletion of Mn at depth within the anoxic pore waters of Loch Duich is probably due to the precipitation of a finely disseminated manganous carbonate phase, which is too low in concentration to be detected by X-ray diffraction techniques or bulk chemical techniques. Thus, although Mn is present in anoxic pore waters principally as labile inorganic complexes, the solubility of Mn in recent coastal sediments such as Loch Duich can be considered to be controlled indirectly by the decomposition of organic matter and the resulting changes in pE and alkalinity. The surface excess of dissolved Mn being due to the dissolution of Mn(IV) as Mn(II) across the oxic - anoxic redox boundary which then either recycles within the top five centimetres of the sediment or diffuses down. The

downward diffusing Mn(II) is removed from solution as finely disseminated manganous carbonate due to interaction with carbonate anions produced during sulphate reduction. This model explains the observed profile in total dissolved Mn.

Application of trace metal pore water results from Loch Duich to the problem of the geochemical composition of shallow water Mn nodules

Ferromanganese nodules, concretions and encrustations are widespread features in many nearshore marine environments including the Baltic, Barents and Kara seas (Man heim, 1965 as quoted in Calvert and Price, in press), the Black Sea and in the region of Loch Fyne, Scotland (Calvert and Price, 1970).

Shallow water marine nodules characteristically have a Mn-rich core with a Mn/Fe ratio of between 1 and 45 which is also enriched in Co and Ni and an Fe-rich rim, often very thin, which is enriched in Zn and Pb (Calvert and Price, 1970). This geochemistry contrasts with that of open ocean nodules, which contain a Mn/Fe ratio of 0.9 - 1.7 and are enriched in Co, Ni, Cu, Pb and Zn throughout the nodule (Mero, 1962). In the sediments of Loch Fyne only those nodules which are present on the surface of the sediment contain the Fe-rich rim, while a number of micronodules are present a few centimetres down within the sediment which contain only the Mn hydroxy-oxide phase (Calvert and Price, 1970). Although there is a controversy as to whether open ocean nodules are basically volcanic or diagenetic in origin, it is generally agreed that shallow water nodules are diagenetic in origin and form as a result of the redistribution of non-detrital Mn phase, principally the precipitation of upward diffusing Mn(II) as Mn(IV) in the upper oxic layers of the sediment.

In order to explain the relative concentrations of Mn, Fe and the trace metals, Ni, Co, Pb and Zn in shallow marine nodules, it has been suggested that the trace metals have been removed from the pore waters and fixed as sulphides before they can become incorporated into Mn nodules (Cheney and Vredenburgh, 1968; Man heim, 1965 as quoted in Calvert and Price, in press). However, data for the relative concentrations of Fe, Cu, Zn, Co, Ni and Mn in the pore waters of Loch Duich (this study) and Loch Fyne (Duchart et al., 1973) show that there is generally a higher concentration of Fe, Cu and Zn than Co and Ni in anoxic pore waters, and thus it is not possible to explain the depletion of the core of Mn nodules in Zn, Pb and Fe as being due to the relative absence of these metals in the pore waters.

The distribution of Fe, Zn, Co and Ni in Mn nodules is probably due to the form in which they are present in the pore waters, and thus their availability for incorporation within nodules. Mn is present principally as labile inorganic Mn(II) complexes in anoxic pore waters, while Fe, Zn and Cu are bound to organic chelates. All of these metals are present in concentrations greatly in excess of that found in the overlying sea water, and will tend to diffuse upwards from the reducing pore waters towards the surface. As soon as Mn(II) diffuses across the oxic - anoxic redox boundary it will tend to precipitate as the Mn(IV) hydroxy-oxide phases characteristic of Mn nodules. Such a reaction accounts for the presence of Mn micronodules a few centimetres down in the sediment of Loch Fyne (Calvert and Price, 1972), Mn enrichments in the surface of certain Pacific Ocean (Lynn and Bonatti, 1965) and Norwegian fjord (Taylor, 1974) sediments. Fe, Zn and Cu which are principally bound to

organic matter in anoxic pore waters (this study) would tend not to coprecipitate with such an inorganic phase (O'Connor and Kester, 1975). The high concentration of Fe relative to Zn, Cu and Pb is due to the presence of preexisting solid Fe oxide phases in the sediment, which become incorporated into the nodules.

The Fe-rich rim to those cores which are exposed at the sediment - water interface is probably brought about by bacterial action. Bacteria are known to concentrate trace metals and particularly trace metal - organic chelates (Wood, 1974) and tend to be associated with the surface of particles (Paerl, 1974). In addition, the greatest number of bacteria are present in the uppermost few centimetres of the sediment (Zobell, 1946). Thus it is likely that the incorporation of organically bound trace metals (Fe, Zn and Pb) by bacteria attached to the surface of Mn nodules, very close to the sediment - water interface, could account for the observed enrichment of Fe, Zn and Pb in the rim of shallow marine Mn nodules. It is thus inferred that Ni and Co do not behave in the same way as Fe and Zn possibly because they are not present in the pore waters as organic chelates; note that the concentration of Ni and Co in the pore waters of Loch Duich was below the detection limits (approximately 5 ppb) of the AA method used.

If this mechanism is valid, then the Fe-rich rim should have a significantly higher proportion of organic matter than the Mn-rich phases, both due to the presence of bacteria and also organic chelating agents within the rim. A similar mechanism involving the biological fixation of Zn and Pb organic chelates from the pore waters has been suggested to explain the surface enrichment of these metals

in the sediments of relatively unpolluted marine environments.

The speciation of Fe, Cu and Zn in reducing pore waters

From the results presented above, it is shown that Fe, Cu and Zn in anoxic pore waters behave in a very different manner from Mn and can be considered together as a group. Whereas dissolved Mn shows a pronounced surface enrichment in those cores where the oxic - anoxic boundary is close to the sediment surface, Fe, Zn and Cu show no simple systematic diagenetic trend in such cores. The analysis of trace metals before and after oxidation on the pore waters of Loch Duich shows a 45 - 69% increase in measured Fe and a 16 - 70% increase in measured Zn. This is proof of the presence of organic chelates of Fe and Zn in the pore waters, the percentage increase representing a minimum value for organically bound metal (Kamps-Nielsen, 1972). There is no significant increase in either Mn or Cu after oxidation. However, there is considerable evidence that Cu is organically bound in sea water (Alexander and Corcoran, 1967; Williams, 1969; Foster and Morris, 1971) and in the anoxic pore waters of Saanich Inlet (Nissenbaum and Kaplan, 1971). It is possible to explain the lack of change in the measured Cu after oxidation as being due to the nature of the Cu - organic chelate; if it has a stability constant only somewhat lower than those of the Fe and Zn chelates, it could be analysed in both the untreated and oxidised fractions (Kamps-Nielsen, 1972).

Within the LMW fraction which constitutes 23 - 44% of the Fe, 42 - 73% of the Zn and 34 - 39% of the Cu, the metal could be present as labile inorganic complexes, non-labile inorganic complexes such as polysulphides or organic complexes and chelates.

The remaining HMW material could contain the metals as inorganic colloids and particles or organic molecules, particularly "humic" substances.

Speciation of Fe, Cu and Zn in LMW fraction

If these metals were present as labile inorganic complexes in solution, as the bulk of the Mn is, then it would be expected that the overall concentration of these metals in pore waters would be controlled by the solubility of the least soluble species, in this case the metal sulphides. Figure 8.11 shows the vertical variation of dissolved Fe as a typical trace metal present in anoxic pore waters compared with the measured concentrations of total dissolved sulphide and total dissolved organic carbon. It can be seen that there is no simple inverse relationship between the solubility of dissolved Fe and dissolved sulphide as would be expected if the precipitation of FeS phases were controlling the solubility of Fe. Additionally, Brooks et al. (1968) calculated the maximum concentration of metal in solution compatible with a total sulphide concentration of 1 mMole/ltr and a pH = 7.7, both fairly close approximations to the levels found in the pore waters of Loch Duich. These show that the calculated maximum solubility of Fe is 3.0×10^{-2} ppb, Zn is 9.0×10^{-7} ppb and Cu is 6.0×10^{-28} ppb, which compares to the range Fe 12 - 52 ppb, Cu 0.5 - 13 ppb and Zn 5 - 380 ppb actually measured in the LMW fraction of the anoxic pore waters from Loch Duich. Thus there is both experimental and theoretical evidence that the concentration of dissolved sulphide does not control the solubility of Fe, Cu and Zn in anoxic pore waters.

It is concluded that virtually none of the Fe, Cu and Zn present

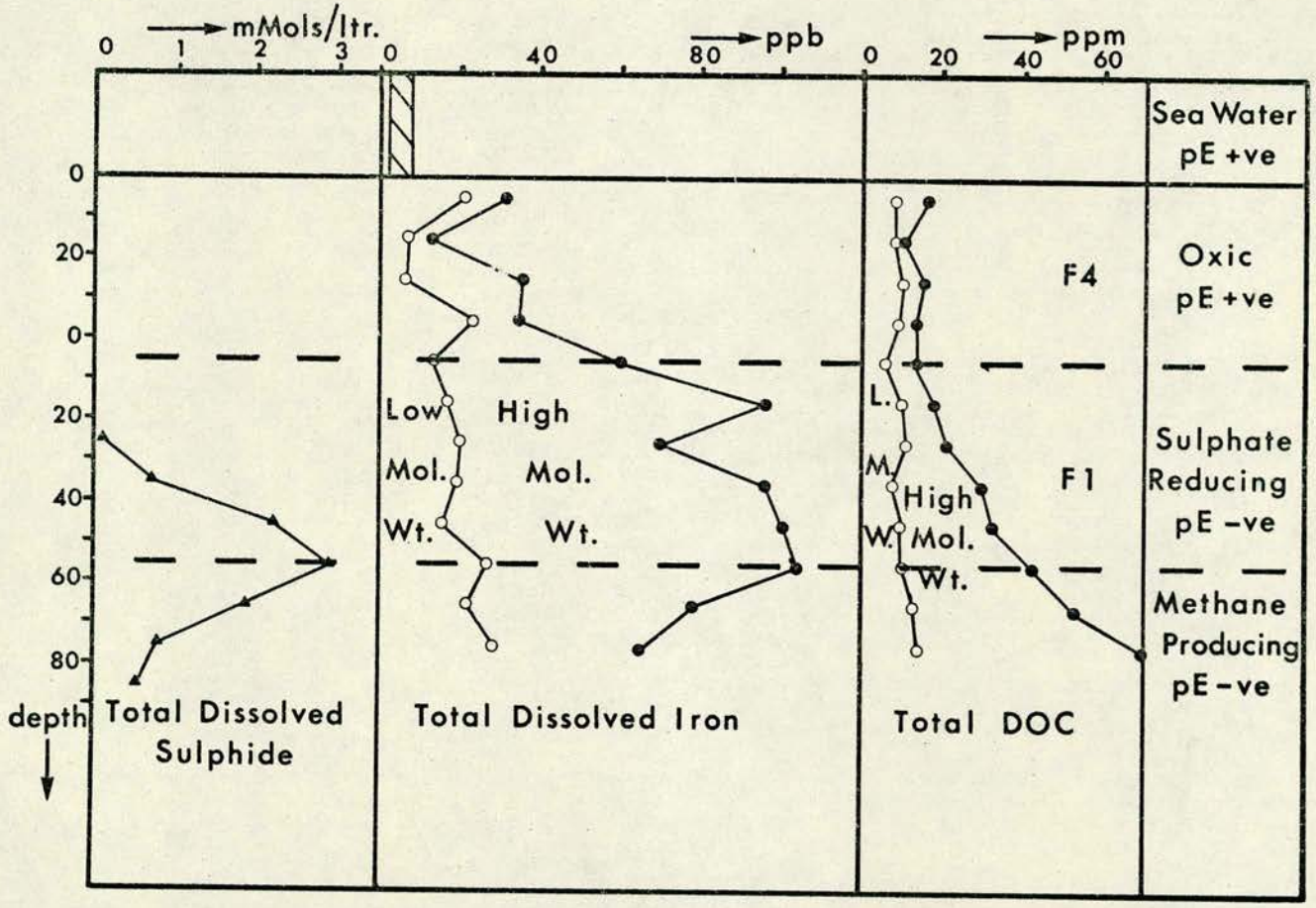


FIG. 8.11 Diagram to Show the Vertical Distribution of a Typical Trace Metal (Fe) and the Principal Species Controlling its Solubility in Anoxic Pore Waters (Data Derived From Cores F1 and F4.)

in the reducing pore waters is present in the form of labile inorganic complexes, and that they are bound to non-labile inorganic and organic complexes and chelates. It has been suggested that organic matter in sediment interstitial waters controls the solubility of trace metals by forming non-labile associations (Brooks et al., 1968; Presley et al., 1972). There is, however, no simple relationship between total DOC and dissolved trace metals in anoxic pore waters. Total DOC is, however, not a good measure of the concentration of complexing and chelating agents in pore waters, since it is known that within the total DOM there are certain fractions which form strong trace metal chelates such as porphyrins and "humics" and other fractions which do not associate with trace metals, for instance hydrocarbons. The analysis of Fe in the humic acid fraction provides experimental confirmation for this observation, since it was shown that up to 20% of the total dissolved Fe is bound to approximately 1% of the total DOM.

The relative importance of certain groups of organic compounds in pore waters is considered as potential chelating and complexing agents. A possible form in which the metals may exist in anoxic pore waters is as complexes with amino acids, compounds which are known to exist in the pore waters of Saanich Inlet (Nissenbaum et al., 1971) and which are capable of forming complexes with trace metals (Saxby, 1969). Gardner (1974) performed a simple calculation to ascertain the importance of organic complexes as the control on the solubility of certain trace metals in reducing pore waters. He used the relative concentrations of a number of amino and simple fatty acids in sea water (Duursma, 1965) and assumed that they are

present in pore waters in a similar ratio to one another and in a concentration 150 times that found in sea water. This multiplication factor represents the ratio of maximum DOC in interstitial waters (Nissenbaum et al., 1971) to average DOC in sea water (Duursma, 1965). He then calculated the trace metal - organic complex activity using the stability constants taken from Sillen and Martell (1964, 1971) at pH = 7.0. Although these calculations necessarily are only very approximate, they show that trace metal complexes with the simple organic compounds examined cannot account for the observed concentrations of trace metals in sulphide rich anoxic pore waters.

Saxby (1969) emphasises the importance of organic chelates in particular porphyrins which have a molecular weight of 500 and upwards as possible molecules to control the solubility of trace metals in sea water. The porphyrins, many of which are derived from enzymes in organisms such as haemin, chlorophyll and vitamin B and as such are thought to be present in sediments and their pore waters. For instance, chlorophyll has been extracted from recent sediments in the Dead Sea and elsewhere (Kaplan and Nissenbaum, 1967 and Corcoran, 1957 as quoted in Saxby, 1969).

Duursma (1970) calculated that Co and Zn could be chelated in sea water by Quinoline-2-carboxylic acid, a compound of MW < 1000 which contains a number of the functional groups present in "humic" substance (Rashid and King, 1970). The calculation was based on a concentration of 2 mgC/ltr, which compares to the concentration of approximately 10 mgC/ltr present in the LMW fraction. This calculation shows that at this concentration of ligand and assuming a pH of 8 and a concentration of Zn of 5 ppb and Co of 0.05 ppb (sea water

concentrations), 99% of the Co and 50% of the Zn are bound as organic chelates.

The concentration of these porphyrins and other chelating agents in the pore waters is, however, unknown, and hence it is not possible to quantify the importance of this group of compounds in controlling the solubility of trace metals in the LMW fraction.

Another group of compounds which are thought to be capable of solubilising trace metals in anoxic pore waters and which would be present in the LMW fraction are the polysulphides. The polysulphides are intermediates in the oxidation of S^{2-} to SO_4^{-2} and S^{o}. They are frequently transitory, but are most stable at pH of 7.0 ± 0.4, a pH range similar to that found in reducing pore waters (Chen and Gupta, 1973). Gardner (1974) calculated that bisulphides and/or polysulphides may be important in controlling trace metal solubilities.

From the data collected on the anoxic pore waters of Loch Duich it is not possible to ascertain whether it is organic chelates such as LMW porphyrins or polysulphides or a combination of both that control the solubility of trace metals in the LMW fraction.

Speciation of Fe, Cu and Zn in HMW fraction

The analysis of the retentate shows that the HMW fraction in the sediment pore waters of Loch Duich contains the major proportion of Fe 56 - 77%, Cu 61 - 66% and Zn 27 - 58% and a high concentration of DOC (11.9 - 69.9 mgC/ltr). Lindberg and Harriss (1974) performed a similar experiment to examine the relationship of Hg and DOM in the pore waters of estuarine sediments from Mobile Bay and the Everglades. In that study four fractions were separated by ultrafiltration, > 100,000, 100,000 - 50,000, 50,000 - 500 and < 500; dissolved Hg and

DOC were measured for each of these fractions. The percentage of total dissolved Hg present in any one molecular weight fraction showed a strong correlation (LRC = 0.94) with the percentage of total DOC in that same fraction. It was thus inferred by Lindberg and Harriss that Hg in sediment pore waters is bound with DOM.

Schindler et al. (1972) extracted sediment and a sample of the overlying lake water from a south Georgia fishpond, a stagnating lake system. After a number of days, samples of the water close to the sediment - water interface were extracted and passed through 5 ultrafilters: 100,000, 50,000, 10,000, 2,000 and 500. The retentate behind each ultrafilter was analysed for Fe, Mg, Zn, Mn and DOC. The total concentration of Fe, Mg and Mn increased with time and appeared to be associated principally with the 10 - 50,000 molecular weight fraction. Although they suggest that this mobilisation of metals during reduction is caused by trace metal - organic chelates released from the sediment, they note that it is possible that metals associated with inorganic colloids such as clays could produce a similar molecular weight distribution. Similarly, the association of trace metals in the HMW fraction in the pore waters of Loch Duich sediments could be due in part to the removal of trace metals from a clay by the action of phosphoric acid used in the analytical method.

Additional experimental evidence for the presence of trace metal - organic chelates is provided by the analysis of the acid insoluble humic acid precipitate. This contains 0.3% by weight of Fe, which is a minimum value because it is known that mineral acid will tend to displace trace metals from humic acid chelates. The "humic" fraction in the pore waters of Saanich Inlet which were

separated by dialysis and lyophilisation also contained 0.3% Fe as well as 0.2% Cu, 0.6% Zn and 0.01% Mn; note that Fe, Cu and Zn are present in this fraction in approximately similar concentrations and in a far higher concentration than Mn.

The HMW fraction of the organics in the pore waters contains a large proportion of "humic" substances, principally fulvic acid, humic acid and melanoids (Chapter 6.6). These "humic" compounds are well known to act as chelators of trace metals in soils (Manskaya and Drozdova, 1968; Kahn, 1969; Schnitzer, 1967; Schnitzer and Kahn, 1972), in natural waters (Shapiro, 1964; Gjessing, 1970), and in marine sediments (Pillai et al., 1971; Rashid, 1971; Desai et al., 1972; Prakesh, 1973). These are the likely compounds within the HMW fraction to bind the trace metals as chelates. Trace metals tend to form complexes and chelates in a definite order of stability for a number of different ligands: Cu > Zn > Fe > Mn (Irving and Williams, 1948). Khan (1969) and Schnitzer (1969) examined the sequence of the stability of trace metals for humic and fulvic acids respectively extracted from soils and found that their results were in broad agreement with the Irving - Williams series, Fe > Cu > Zn > Mn (Kahn, 1969) and Cu > Fe > Zn > Mn (Schnitzer, 1969). In all these results it is noted that Mn forms the least stable of the trace metal chelates with "humic" substances and that this may be the explanation why Fe, Cu and Zn seem to be present as organic chelates while Mn behaves as labile inorganic complexes.

Production of pyrite in anoxic sediments

It is characteristic of many anoxic sediments that they are black in colour, which is due principally to the presence of meta-

stable iron sulphide species such as mackinawite $FeS_{0.9}$, greigite Fe_3S_4 and hydrotroilite FeS (Berner, 1967; Goldhaber and Kaplan, 1975), which then convert in time and with the addition of further sulphur into the stable sulphides, pyrite FeS_2, marcasite FeS_2 and pyrrhotite $Fe_{1-x}S$. The metastable sulphides are formed by the reaction of dissolved sulphide, produced by the metabolic decomposition of sea water sulphate and Fe. The problem which the data from this study can help to answer is the form of the Fe within the sediment which becomes fixed as iron sulphides.

Several studies have shown that reactive Fe is supplied to the sediment mainly as adsorbed coatings of colloidal ferric oxides, such as haematite and goethite on detrital clays and silt grains. In addition, finely crystalline iron-containing chlorites are also generally reactive (Berner, 1971). From isotopic evidence, the major incorporation and fixation of sulphides into the sediment takes place in the upper few centimetres where there is a free exchange between sea water sulphate and the interstitial waters where sulphate reduction is occurring (Goldhaber and Kaplan, 1975). This reaction, involving the fixation of dissolved sulphide in the sediment as iron sulphides, could be due to (1) a simple ionic precipitation between dissolved Fe and sulphide in the pore waters (Roberts et al., 1969), (2) a microbiologically catalysed precipitation of these two dissolved species (Hallberg, 1972) or (3) reaction between dissolved sulphide and solid Fe oxides without an intermediate dissolved Fe (II) phase (Berner, 1971; Goldhaber and Kaplan, 1975). Evidence is presented here to suggest that this latter process is the most likely.

Figure 8.11 shows the variation of dissolved Fe and sulphide

within the interstitial waters of an anoxic core (F1). There is no correlation between these two species, in particular the level in the sediment where there is maximum sulphide concentration does not correspond to a minimum value of dissolved Fe as would be expected if they were reacting directly to form a precipitate. In addition, calculation has shown that the maximum concentration of ionic Fe(II) in the pore waters at a pH of 7 and with a total dissolved sulphide concentration of 1 mMole/ltr is 0.003 ppb, approximately 0.003% of the total dissolved Fe (Brooks et al., 1968). It is thus concluded that the remaining Fe (> 99.9%) in anoxic pore waters is present as non-labile organic chelates (this study) and is not available for precipitation with dissolved sulphide. Note however that such considerations are only valid for the pore waters as extracted. It is possible that the chemistry of the pore waters in very close contact with the sediment could be different and that reactions between dissolved Fe and dissolved sulphide could take place.

However, the most probable species in the sediment which could provide the source of Fe for reaction to form sulphides are thus solid iron oxides (Kaplan et al., 1963). Goldhaber and Kaplan (1975) in a review article on the sulphur cycle within marine sediments suggest that sulphide is fixed in the sediment by reaction with iron hydroxy-oxides very close to the sediment - water interface to form mackinawite, which then reacts with free sulphur to form greigite and pyrite. The evidence presented in this study tends to confirm such a mechanism.

8.5 Summary

1) The geochemistry of Mn in the pore waters of recent sediments both

oxic and anoxic is significantly different from that of Fe, Cu and Zn.

2) Mn is present in the pore waters of anoxic reducing sediments principally as labile inorganic complexes.

The observed pore water profile of Mn can best be explained by a diffusion model which is controlled indirectly by the metabolic breakdown of organic matter. Within the top few centimetres Mn(IV) is converted to Mn(II) across the oxic - anoxic redox boundary. This large excess of dissolved Mn(II) is either recycled up to the surface or it diffuses down, where it is removed in combination with alkalinity produced during sulphate reduction as a manganous carbonate. Similar models have been used to explain the dissolved Mn profile in regions with high concentrations of Mn (Li et al., 1969; Calvert and Price, 1972). The data presented here suggests that this model is also valid in regions of low Mn concentrations (0.04% in the sediment).

3) Fe, Cu and Zn are present in the pore waters in a non ionic form, a large fraction being organic chelates. The metals found in the LMW (MW < 1000) fraction (Fe 23 - 43%, Zn 42 - 73% and Cu 34 - 39%) are probably present as LMW organic chelates such as porphyrins and/or as polysulphide complexes. Most of the metals found in the HMW fraction are chelated to "humic" substances although it is possible that some are present in inorganic colloids and particles.

4) Although the presence of trace metal - organic chelates has been demonstrated, there is no simple relationship between the dissolved trace metals and total DOC because certain fractions of the DOM are more important trace metal binders than others.

5) The chemistry of Fe, Cu and Zn in sediment pore waters is thought

to be controlled by chelation with organics. However, the processes which are occurring are very complex including concentration and excretion of metals and organic matter by both macro and microorganisms, competing reactions between different organic chelates as well as complex inorganic equilibria. Despite these complexities, it is possible to explain certain aspects of the observed sediment geochemistry of these metals in terms of diagenetic reactions involving trace metal - organic chelates.

CHAPTER 9

TRACE METALS IN THE SEDIMENTS

9.1 Introduction

Previously it has been observed that there is a trace metal enrichment in the surface sediments of a number of apparently unpolluted fjords in Norway and Scotland. Price (1973) and Taylor (1974) suggested that this enrichment could be due to natural diagenetic recycling processes rather than to direct pollution. With the detailed data available on the pore water and sediment geochemistry of Loch Duich, it is possible to consider the mechanisms which could result in surface enrichments of trace metals.

9.2 Methods and results of the analysis of trace metals in the sediment

Oven dried ($80^{o}C$) and ground sediment samples were analysed for the trace metals Fe, Mn, Cu, Zn, Pb and Rb by an X-ray emission method similar to that used by Taylor (1974) and Davies (1976) (see Appendix B). A correction was made for the dilution effect of residual sea salt in the sediment using the value obtained from the water content.

The results of these analyses (Table 9 I and Figures 9.1 - 3) show that the surface sediments are enriched in lead and zinc for all the reducing cores analysed (A2, A7 and F1) while showing less enrichment in the oxic cores A4 and F4. The surface enrichments of zinc compared to the concentration found in the sediment at a depth

Table 9 I

Concentration of trace elements in the sediment of Loch Duich

Core and depth (cms)		Rb (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Fe (%)	Mn (%)
F4	0	113	115	23	47	4.5	0.04
	5	108	110	20	33	4.3	0.04
	10	116	110	20	38	4.3	0.04
	15	118	104	22	33	4.3	0.04
	20	116	95	20	32	4.3	0.04
	25	130	103	27	36	4.4	0.04
	30	124	95	27	33	4.6	0.04
	35	116	87	22	28	4.6	0.04
	40	111	79	20	34	4.7	0.03
						Fe_2O_3(%)	
A4	0	104	123	28		6.05	0.04
	10	120	98	15		6.18	0.04
	20	120	75	16		6.08	0.05
	30	120	87	21		6.44	0.04
	40	118	83	17		6.38	0.04
	50	131	108	42		7.32	0.05
	60	110	78	13		5.97	0.04
	70	105	73	6		5.61	0.04
A7	0	117	121	10		6.05	0.06
	10	121	151	22		6.83	0.06
	20	117	137	22		6.87	0.06
	30	98	84	4		6.06	0.07
	40	113	101	18		6.73	0.08
	50	109	95	22		6.63	0.07
	60	108	93	15		6.75	0.07
	70	112	88	14		6.54	0.07
F1	0	113	164	29	57	5.0	0.06
	5	112	145	27	50	4.7	0.06
	10	115	154	36	55	4.9	0.05
	15	113	151	28	54	4.8	0.06
	20	114	152	31	53	4.9	0.05
	25	113	144	26	49	4.8	0.06
	30	106	135	22	54	6.5	0.06
	35	117	148	32	53	4.8	0.06
	40	114	138	26	41	4.8	0.05
	45	115	126	27	43	4.9	0.05
	50	111	125	30	43	4.9	0.06
	55	112	122	28	40	4.9	0.06
	60	110	111	27	36	4.4	0.06
	65	111	107	27	34	4.6	0.06
	70	102	96	20	39	4.5	0.05
	75	108	97	28	26	4.9	0.06
	80	102	97	20	64	4.9	0.05

continued

Table 9 I (continued)

Core and depth (cms)		Rb (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Fe (%)	Mn (%)
A2	0	114	118	12	34	4.8	0.06
	10	117	143	28	38	4.7	0.06
	20	120	125	25	36	4.9	0.06
	30	107	101	17	30	4.7	0.05
	40	103	92	21	28	4.9	0.06
	50	123	90	18	30	4.7	0.06
	60	110	93	15	27	4.9	0.06
	70	106	88	18	30	4.7	0.06
	80	105	86	14	26	4.8	0.05

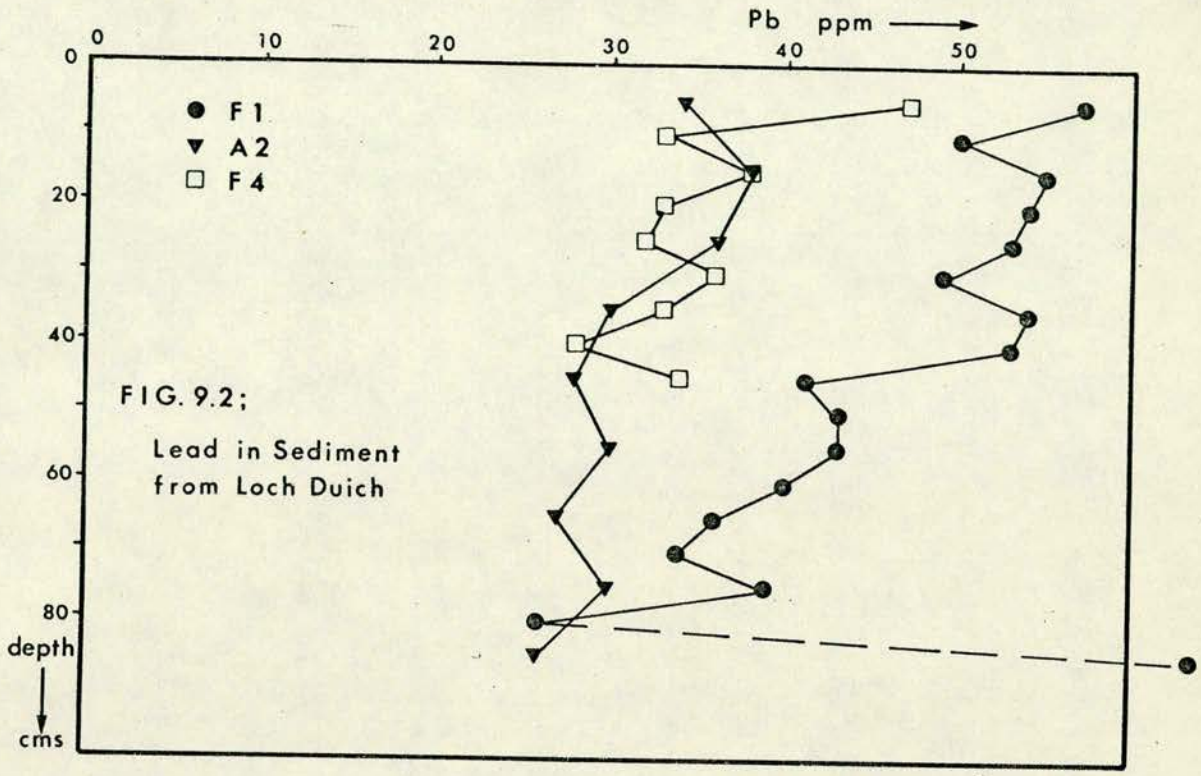


FIG. 9.2;
Lead in Sediment
from Loch Duich

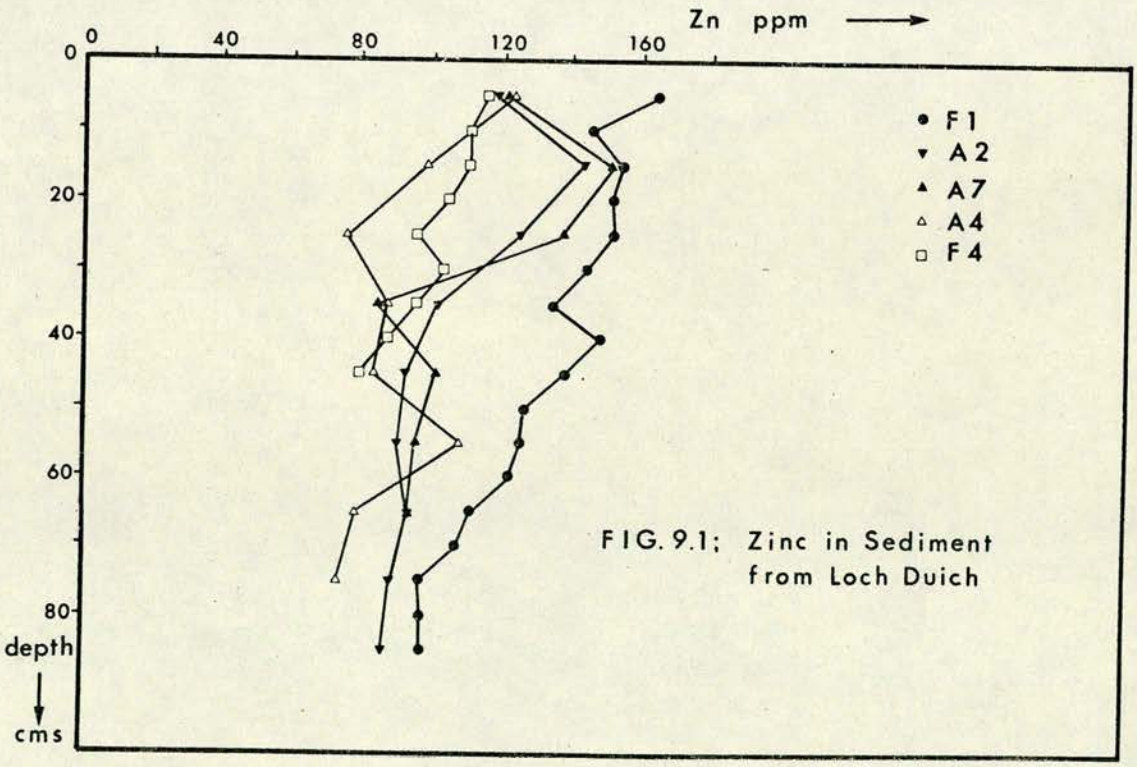


FIG. 9.1; Zinc in Sediment
from Loch Duich

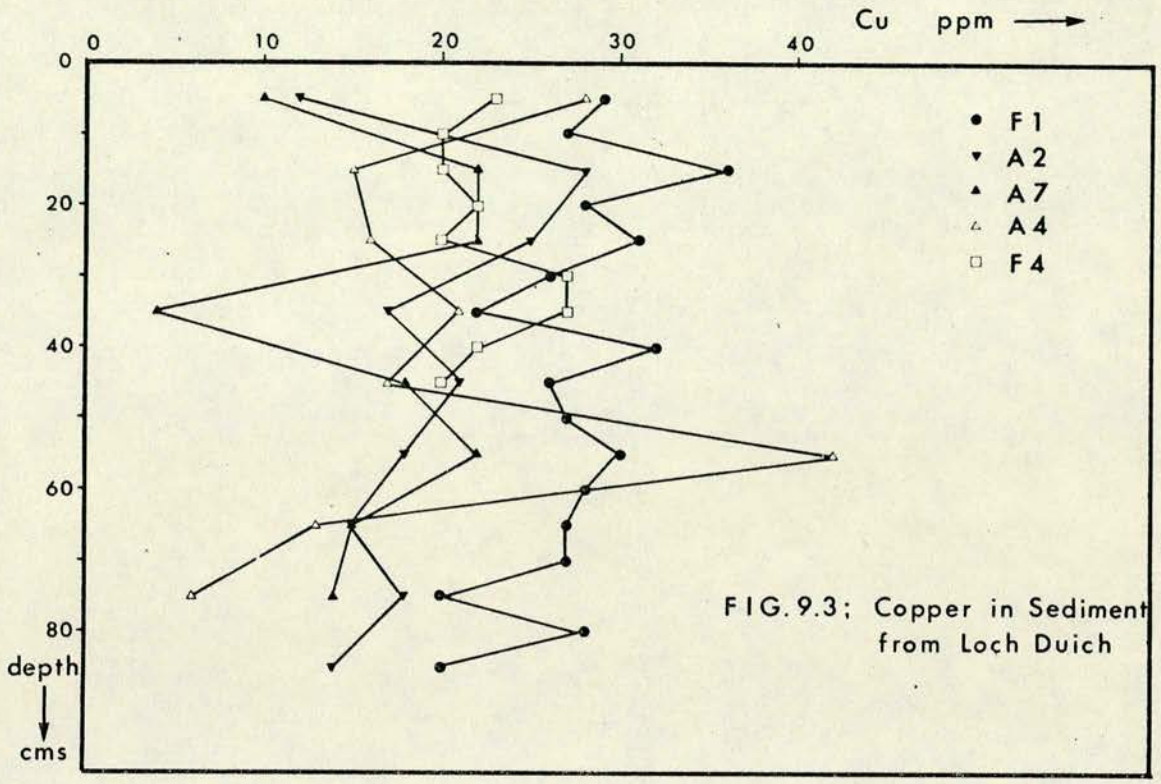


FIG. 9.3; Copper in Sediment from Loch Duich

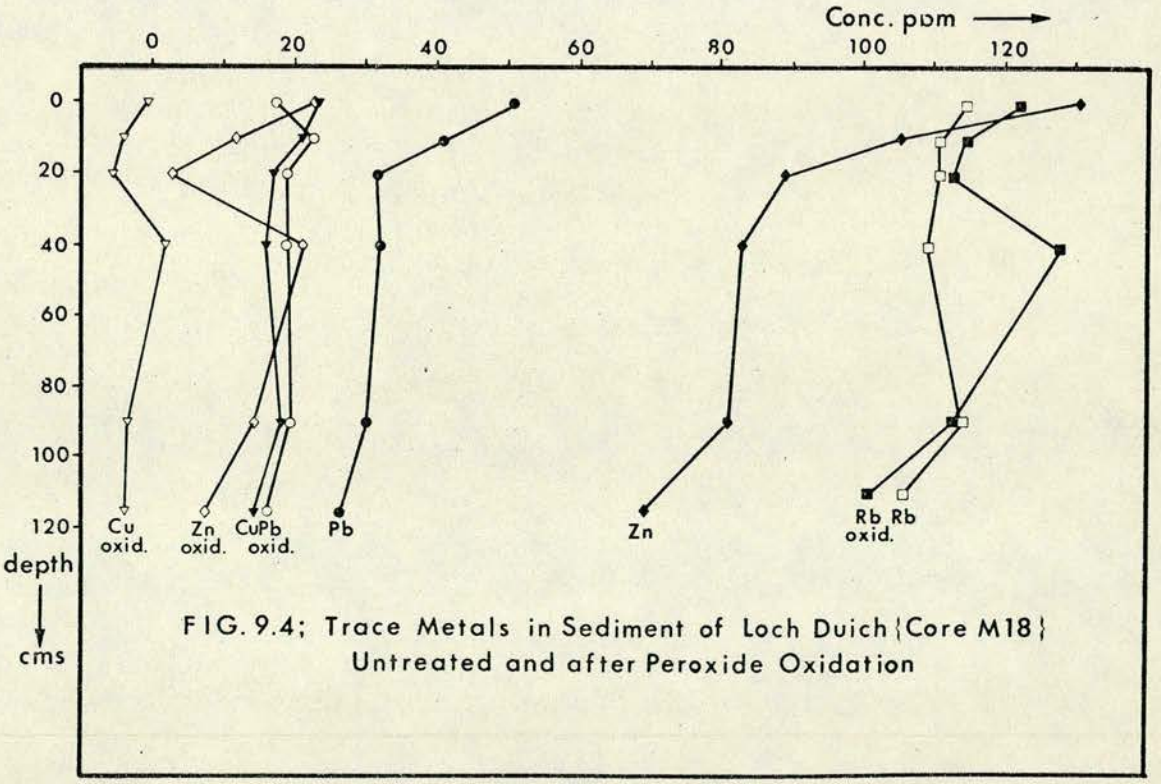


FIG. 9.4; Trace Metals in Sediment of Loch Duich (Core M18) Untreated and after Peroxide Oxidation

of 60 - 80 cms* (Figure 9.1) are A2 143 ppm ← 90 ppm, A7 151 ppm ← 90 ppm, F1 164 ppm ← 97 ppm, A4 98 - 123 ppm ← 73 ppm and F4 115 ppm ← 79 ppm. Similarly, the concentration of lead found at the surface compared to that found at depth (Figure 9.2) is A2 38 ppm ← 28 ppm, A7 not measured, F1 57 ppm ← 26 ppm, A4 not measured and F4 33 - 47 ppm ← 34 ppm. The values obtained for Cu are somewhat erratic, and thus it is not possible to ascertain whether there is a surface enrichment or not. Fe and Mn are not enriched in the surface sediments, although it is probable that there is a thin layer (approximately 1 cm) at the surface of the sediment which was not sampled during the coring operation. The trace metal enrichment of Pb and Zn is not related to any simple change in lithology or grain size, since the sediments of Loch Duich have a constant lithology and grain size distribution within the depth of the core sampled (Chapter 3).

Samples of dried sediment from core M18, a reducing core from the central basin, were chemically treated by boiling with acidified hydrogen peroxide solution until the sediment appeared to be bleached and no further foaming occurred. The sediment was then analysed for trace metals by the same X-ray emission method as before. The results before and after treatment are shown in Figure 9.4. This chemical treatment will remove most of the non-lithogenous fractions, organics, oxides, sulphides and adsorbed trace metals, leaving only the most resistant phases.

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* except for F4, which was only sampled down to 40 centimetres.

None of the rubidium was lost in this treatment, suggesting that the lithogenous phase in the sediment was not attacked.

Both Pb and Zn were reduced by this treatment, Pb from 30 - 50 ppm to 20 ppm and Zn from 70 - 130 ppm to 10 - 20 ppm. The trace metal surface enrichments for Pb and Zn which were clearly visible on the untreated sample were completely removed, showing that all the enrichment was present in the non-lithogenous fractions. The concentrations of Fe, Mn and Cu were also reduced substantially by this treatment from 6.1 - 6.7% $\longrightarrow$ 4.2 - 4.8%, from 450 - 530 ppm $\longrightarrow$ 140 - 220 ppm and from 14 - 23 ppm $\longrightarrow$ 4 - 12 ppm respectively.

Although all the trace metal enrichment is present in the non-lithogenous fraction, there is no simple correlation with total organic carbon, as a measure of the organic matter. Neither is there a correlation with iron and manganese, usually taken as a measure of the oxide/sulphide phase which might be expected to coprecipitate trace metals in sediments (Jenne, 1968).

There are considerable problems in the use of further chemical treatments to attempt to differentiate between the organic and inorganic fractions of the non-lithogenous phase of trace metals. It is not possible to use non-acidified hydrogen peroxide, since although it destroys the organic matter, as can be seen by the results for iodine and carbon (Chapter 7.5), there is no reduction in trace metals, probably because on oxidation, any trace metal - organic complexes present break down to form a trace metal oxide phase which remains in the solid portion of the sediment.

Similarly, it is not possible to measure any oxide phase which might be present in the sediment, since the most common reducing

agents used, dithionite-citrate (Mehta and Jackson, 1960) and hydroxylamine/acetic acid (Chester and Hughes, 1967), both remove a certain unknown portion of organic matter as well as the oxide phase.

Other work on trace metal surface enrichments

Similar trace metal enrichments have been found in a number of localities, Mofjord and Bolstadfjord, Norway (Taylor, 1974), Byfjord (Olausson, 1975), Loch Fyne (Price, 1973), the Baltic Sea (Erlenkeuser et al., 1974) and in several of the basins from the California borderlands (Bruland et al., 1974). Table 9 II shows surface concentration of the trace metals Pb, Zn and Cu for all of these basins, together with the concentration of metal at the depth at which no further enrichment is observed. The date of the lowest point of trace metal enrichment is shown where it has been measured. The final column shows the change in concentration between the surface level and the base level concentration, the magnitude of the trace metal enrichment.

Loch Duich, Mofjord, Bolstadfjord and Loch Fyne are all located in areas where there is no obvious local source of trace metal pollution, while Byfjord, the Baltic Sea samples and those collected off the coast of California are adjacent to areas which are highly populated and industrialised.

It is to be noted that the Baltic Sea samples show a significantly greater surface enrichment in Cu, Zn and Pb than do any of the other samples, either those where pollution is claimed as being the source of the trace metal enrichment, such as off the coast of California (Bruland et al., 1974) and Byfjord (Ollausen, 1975) or in those areas where another mechanism has been suggested to explain the trace

Table 9 II

Trace metal enrichments in recent marine sediments

Location	Conc at depth	Surface conc.	Trace metal enrichment	Date of increase	Reference
ZINC					
Mofjord	120	140	20	-	Taylor, 1974
Bolstadfjord	100	180	80	-	..
Baltic Sea	120	340	220	1800	Erlenkeuser et al., 1974
Byfjord (2)	35	55	20	1955	Ollausen, 1975
Loch Duich	97	164	67	-	This study
S. Monica (1)	100	150	50	1930	Bruland et al.,
S. Barbara(1)	100	130	30	1930	1974
San Pedro (1)	90	140	50	1920	..
LEAD					
Mofjord	30	75	45	-	as above
Bolstadfjord	26	75	49	-	
Baltic Sea	20	82	62	1800	
Byfjord (2)	0	13	13	1950	
Loch Duich	30	57	27	-	
S. Monica	10	30	20	1900	
S, Barbara	10	30	20	1930	
San Pedro	10	50	40	1920	
COPPER					
Mofjord	24	28	4	-	as above
Bolstadfjord	20	30	10	-	
Baltic Sea	35	70	35	1800	
Byfjord (2)	5	5	0	-	
Loch Duich	20	20	0	-	
S. Monica	40	55	15	1940	
S. Barbara	30	30	0	-	
San Pedro	40	50	10	1950	

(1) Inferred enrichment based on the metal/Al ratio. The uncorrected enrichment is lower or not present at all.

(2) analysed by acid extraction.

metal enrichment (Price, 1973; Taylor, 1974). The sediment samples from the Baltic Sea show an anomalously low surface C^{14} date, and this, together with presence of visible coal fragments, has caused Erlenkeuser et al. (1974) to suggest that this surface enrichment is due at least in part to particles of coal and fly ash derived from industrial activity on the adjacent coast. This coal ash is known to contain very high concentrations of trace metals as well as yielding an anomalously low C^{14} date.

Bruland et al. (1974) argue that the trace metal enrichments off the coast of California are due entirely to pollution. The evidence for this is that the depth at which trace metal enrichment occurs coincides approximately with the introduction of the automobile to California. Many of the suggested trace metal enrichments such as those for Ni, Co and Cd are perhaps not justified from the data presented, while other elements, including V, Cu, Ag and Cr, show definite trace metal enrichments in only one or two of the three basins analysed. Only Pb and Zn show definite surface enrichment in all the cores examined. A comparison is drawn between the Santa Barbara, Santa Monica and San Pedro basins, which are put forward as examples of basins which are polluted, and sediment from the Soledad basin, which derives its sediment from an unpolluted area. Although it is true that none of the sediment samples from the Soledad basin show surface enrichment (except for Zn, which is explained as due to contamination from the galvanised Zn box corer), the sediment from these two regions is geochemically and lithologically very different. The Al content of the sediment of the Soledad basin is approximately 2%,

while that from the California borderlands is 6%, the TOC in the Soledad basin is 6% compared to 2 - 4.5% in the other basins and the calcium carbonate content is 20% compared to 4 - 16% for the other basins. It is also likely that the grain size distribution between the cores from these two areas is also very different, although no data is presented. Any natural diagenetic process which may occur to redistribute Pb and Zn in the sediment is likely to be controlled by the nature of the trace metal input, metabolic reactions occurring within the sediment, exchange reactions between the sediment and its pore waters, the rate of movement of dissolved trace metals through the sediment and the sedimentation rate. It is likely that many of these parameters will be different in the Soledad basin when compared to the other three basins, and thus it is considered unwise to use such a simplistic view of trace metal enrichment when comparing two regions with such different lithologies.

9.3 Possible sources of anthropogenic input of trace metals to explain the enrichments in the surface sediments of Loch Duich

There is no local industry or mine in the immediate region of Loch Duich which could possibly be the source of the trace metal enrichment by direct pollution. It is thus necessary to examine the possibilities of trace metals being transported in from more distant industrial regions.

It has been suggested that a considerable anthropogenic input could be brought in as fine particles in the air and washed out in the rain. Ruhling and Tyler (1973) measured the trace metal content of mosses throughout Scandinavia and showed an increase in trace metal content, particularly Pb, as one moved southwards across

Scandinavia. However, there were no analyses performed on any detrital elements, and hence it is not possible to differentiate from the data presented between an increase in anthropogenic trace metals and a simple increase in the total flux of particles both natural and anthropogenic. There is also no data provided on the prevailing wind directions in this region, particularly the wind direction on those days on which a significant rainfall occurred, a measurement which Little and Martin (1974) emphasise is of great importance in the measurement of the direction of derivation of airborne pollutants. Figure 9.5 represents a wind rose derived from unpublished data (Scot. Met. Office) showing the wind direction at Duirnish on those days in 1973 and 1974 on which it rained more than 5 mm at Achnagart. Both these meteorological stations are close to Loch Duich, Achnagart being in Glen Shiel while Duirnish is on the shores of Loch Carron, approximately 10 miles from the mouth of Loch Duich (Fig. 2.1). The majority of rain which fell on the catchment area of Loch Duich was brought in on winds which came from between south and west. The nearest major industrial region from which trace metals such as those shown to be enriched in Loch Duich could be derived is the Americas and possibly to a lesser extent N. Ireland. Thus it is suggested that it is unlikely that this enrichment is derived from any direct source of air-borne pollution.

Murozumi et al. (1969) analysed the lead levels in snow from Greenland and found that there is a considerable enrichment in the most recent surface strata. This is interpreted as being due to particles of lead being carried up into the upper atmosphere and deposited with snow. Although evidence that such pollution exists

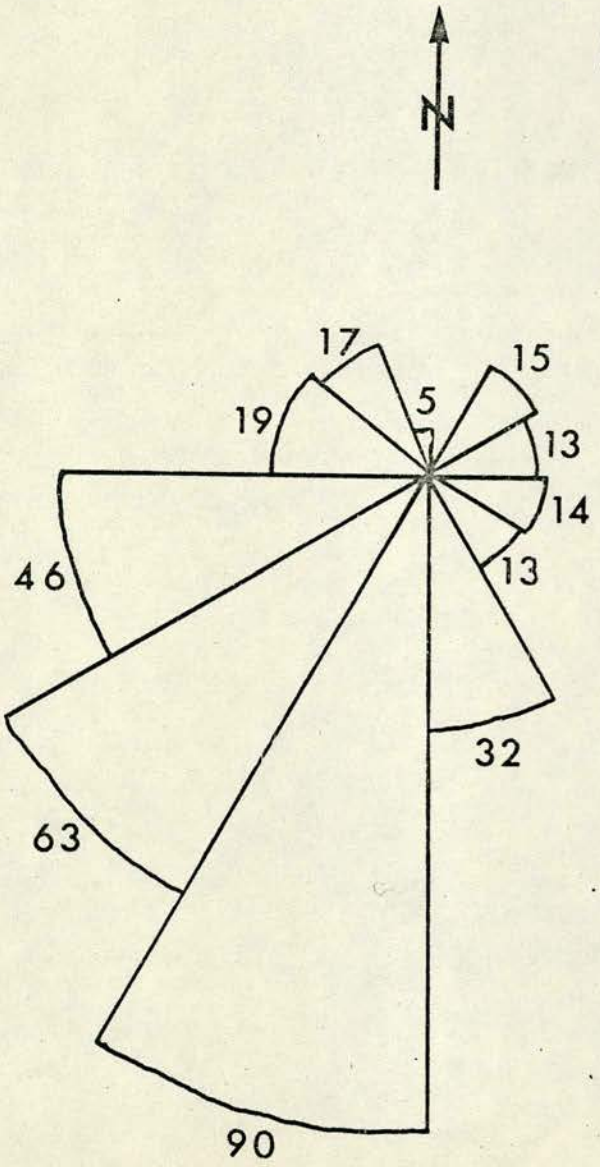

FIG.9.5; Wind Rose at Duirnish on days when it Rained more than 5mm. at Achnagart

is very good, it is very difficult to estimate whether the flux from such a source into the sediment catchment area of Loch Duich would be sufficient to cause the observed lead enrichment. In addition, Duce et al. (1975) compared the lead enrichment levels from air-borne particulate matter in Greenland and in Antarctica and found them to be comparable. Since the major sources of lead pollution are in the highly industrialised northern hemisphere and there is relatively little exchange of air masses between the northern and southern hemispheres, they questioned whether the lead enrichments found in the surface layers of snows were natural or pollution. Pierson et al. (1973) analysed for trace metals in the airborne particulate matter deposited on a hillside in the lake district of England (Wraymires). The prevailing wind, as on the west coast of Scotland, is south-westerly, however there is considerable heavy industry relatively close, Barrow in Furness is 30 km to the south. They found that the particulate matter showed a considerable excess of Pb and Cu but no excess of Zn over that present in terrigenous particulate matter using Sc as a measure of the detrital fraction. If this is a general characteristic of air-borne particulate matter over Britain, and if air-borne pollution is the source of Pb and Zn enrichments in the surface sediments, then it is necessary to explain why the air-borne particles are enriched in Pb and Cu but not Zn, while the surface sediments are enriched in Pb and Zn.

Water-borne pollution

The majority of the sediments deposited in the central basin of Loch Duich are derived from detritus brought in from the sea. It is thus possible that the excess flux of Pb and Zn has been brought into

the area as water-borne particulate matter. Unfortunately, the data available on this subject is very limited. Monitoring of radioactive pollutants by government scientists (pers. comm.) has shown that a considerable quantity of Cs^{137} is present in the surface sediments off the west coast of Scotland, which is thought to be derived from sources in the Morecambe Bay area of N,W. England. Such movements could also move other pollutants such as Pb and Zn from areas adjacent to industrial Lancashire and deposit them in Loch Duich.

Another possible source of pollution is the erosion of peat bogs in the Northern Highlands, which results in an increased supply of terrestrial "humics". These humics are known to be strong chelators of trace metals and it is possible that they may absorb trace metals from the sea water within the estuary and deposit them as trace metal - humate chelates in the surface sediments. This increased supply of peat could be due to a natural climatic change which has occurred in the post-Flandrian (5000 B.P.) period and which is known to have resulted in the erosion of many of the highland peat areas in Scotland (R. Cornish, pers. comm.) or to peat eroded directly from man's activities such as road cutting, quarrying, etc. If this factor is to be considered important in the Loch Duich area, then it is necessary to explain why the trace metal enrichment in the Loch Beg area, where most of the organics are thought to be terrestrially derived and flocculated humics, is much less than the enrichment in the central basin, where there is a higher proportion of marine derived organics.

All of these possible sources of pollution are likely to have some effect on the levels of trace metals in the recent sediments of

Loch Duich. The relative importance of these types of pollution is not, however, known. In addition, it is noted that the N.W. coast of Scotland and the W. coast of Norway are two of the least polluted areas of western Europe. Since pollution tends to decrease with increasing distance from its source (Little and Martin, 1974; Ruhling and Tyler, 1973), it is likely that areas close to a major source of industrial pollution should have much higher levels of trace metal enrichment. Although there is a larger surface excess found in the sediments of the Baltic Sea (Erlenkeuser et al., 1974) than in Loch Duich, which is interpreted as being due to direct local pollution, the trace metal enrichments for Pb, Zn and Cu found in the "polluted" sediments off the coast of California and Byfjord are similar in magnitude to those found in the "unpolluted" fjords of Norway and Scotland.

Additionally, the sediments are enriched principally in Pb and Zn, while the air-borne particulate matter shows an excess of Pb and Cu and no excess Zn. If the total surface excess in the basin sediments of Loch Duich is due to anthropogenic input which is not modified by subsequent diagenetic alteration, then the sedimentation rate is approximately 1 cm/yr (i.e. enrichment down to 50 cms and inferred pollution of Pb since approximately 1920), which is very rapid for a coastal marine sediment, particularly since the sediment is derived not from a major river system but from tidal inflow over three relatively shallow sills.

These difficulties can be resolved if the trace metal enrichment of the surface sediments is explained by a natural diagenetic mechanism, such a mechanism has been put forward by Price (1973).

A possible mechanism is set out in detail here and a calculation is made based on data collected in this study to estimate whether it is feasible that Zn could migrate upwards in the sediment pore waters at a rate sufficiently rapid to supply the observed surface excess.

9.4 Diagenetic recycling mechanism to explain the surface excess of zinc (and lead) in recent sediments

Figure 9.6 shows in a diagrammatic form the processes which are thought to take place in the surface 60 cms of the sediment of Loch Duich, and which result in the production of the observed surface enrichment of trace metals, particularly Pb and Zn. The trace metal enrichment of Zn is considered in detail because data is available for its concentration in the sediments and their interstitial waters. It is suggested that Pb behaves in a similar way.

The trace metal excess, which is present entirely in the non-lithogenous fraction, becomes buried as sedimentation continues. During burial a number of microbial processes occur which result in the accumulation of nutrients, sulphide and HMW organics, principally "humics". The nature of these processes is discussed in Chapters 5 and 6. They give rise to a sequence of biogeochemical zones which have been recognised in the pore waters (Chapter 5.2). The HMW "humics" are known to be potentially very strong chelators of trace metals. These "humic" substances solubilise the trace metals from the sediment, thus reducing the trace metal concentration in the sediment to a base level. This HMW "humic" material is present in greater concentration in the lower portion of the core than at the surface, and thus moves upwards by a process of diffusion (and advection), carrying with it bound trace metals. In addition, it has

been established that a considerable fraction of the trace metals Fe, Zn and Cu are bound to the HMW "humic" fraction in the pore waters. Although a simple trace metal diffusion gradient is not observed in the pore waters, the trace metals must also be diffusing upwards because of the large difference in metal concentration between the pore waters and the overlying sea water.

When this organic matter reaches the surface, a large fraction of the organic matter with combined metals is removed from solution by precipitation onto the sediment. In the basin sediments of Loch Duich, this precipitation could be the result of an organic or an inorganic reaction or a combination of both.

It is known that marine organisms extract trace metals from sea water, incorporate them into their body tissue and then excrete then as large faecal particles which become part of the sediment (Lowman et al., 1971). This phenomenon has been examined by laboratory experiments involving the biological amplification of trace metals in the faeces of crabs (Boothe and Knauer, 1972), the excretion of Zn as particulate matter by prawns (Small et al., 1974), the uptake of Zn by benthic marine algae (Gutknecht, 1963) and the incorporation of DOM and trace metals by bacteria (Jones, 1970; Lowman et al., 1971) which are known to be almost exclusively attached to the surface of sediment particles (Paerl, 1974). It is also known that the greatest metabolic activity, the highest concentration of marine benthos and bacteria occur within the first few centimetres of the sediment (Kaplan and Rittenberg, 1963), and hence the maximum precipitation of trace metals might be expected in this region.

Manganese is precipitating as Mn(IV) oxide phases close to the sediment - water interface of the basin sediments of Loch Duich.

This oxide phase is known to be effective in scavenging trace metals out of solution (Jenne, 1968). This is a possible inorganic mechanism for the precipitation of upward diffusing organically bound trace metals close to the sediment - water interface.

The evidence that trace metal surface enrichment is particularly well developed in sediments where the oxic - anoxic boundary is close to the surface of the sediment is ambiguous. There is no trace metal enrichment reported in the surface sediments of Saanich Inlet, an intermittently anoxic fjord (Presley et al., 1972), while Bolstadfjord, with a similar hydrographic regime, has a trace metal enrichment (Taylor, 1974). The surface enrichments of the oxic cores from Loch Beg are less pronounced than those from the central basin cores, although it is noted that these cores differ not only in pE but also in lithology, derivation of sediment and grain size. This ambiguity of results demonstrates how complex the interrelationship of processes in the natural environment is and some of the dangers inherent in taking a simplistic view of the trace metal distribution in the surface metre of the sediment.

Calculation to demonstrate the feasibility of such a recycling mechanism to explain the trace metal enrichment observed in the surface of a typical basin core in Loch Duich

In order to demonstrate the feasibility of a recycling mechanism within the top metre of the sediment, it is necessary to calculate whether the flux due to sedimentary input (F) is comparable to the flux due to the upward diffusion of organically chelated trace metals (J_{Zn}) (Fig. 9.6). In this calculation the values for total sedimentary zinc, the DOC concentration in the HMW fraction and

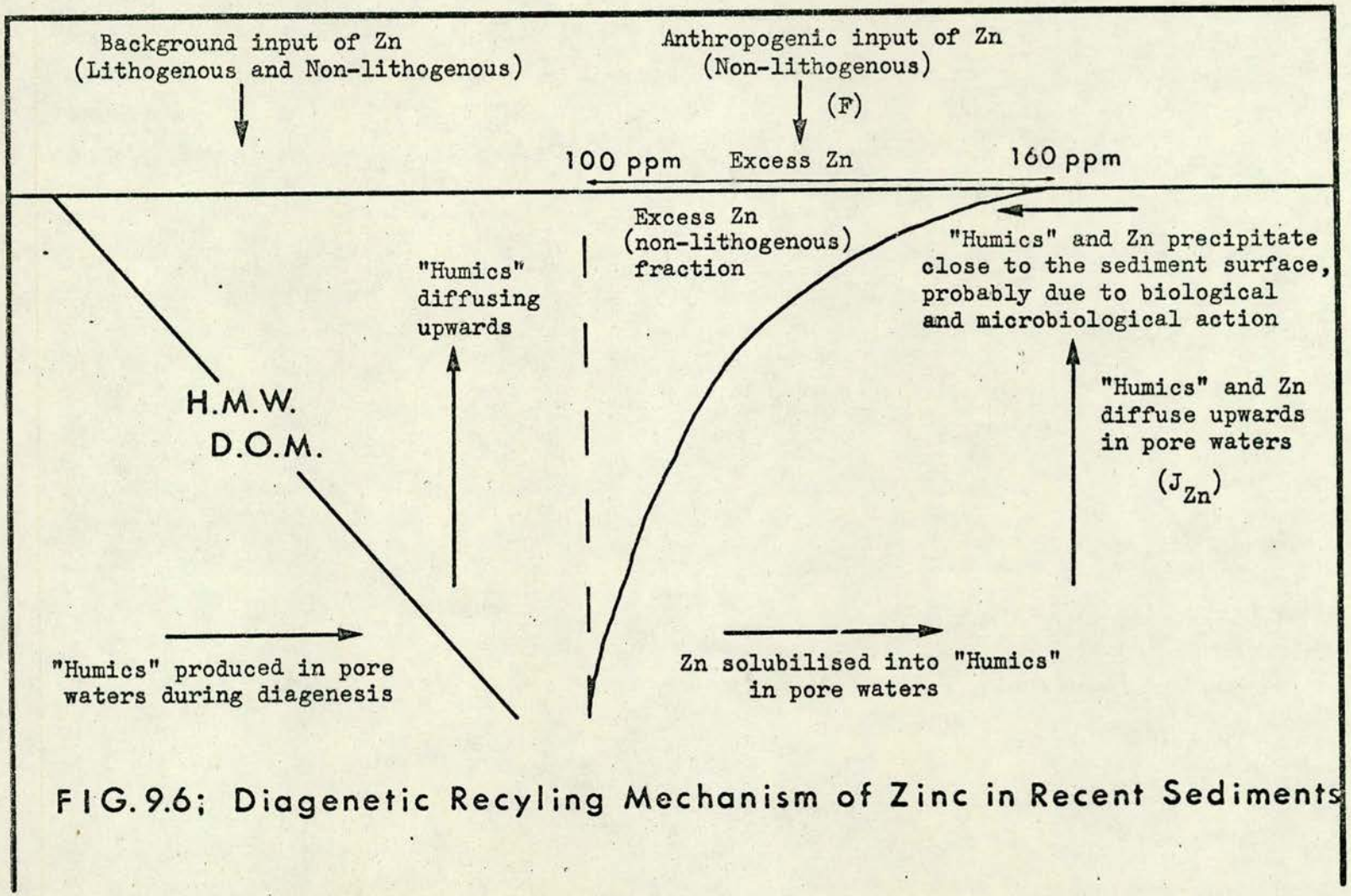

FIG. 9.6; Diagenetic Recyling Mechanism of Zinc in Recent Sediments

porosity are derived from data obtained on core F1.

The values for HMW dissolved Zn and the increase after oxidation in total dissolved Zn are derived from cores A2 and A7. Certain approximations are made in order to perform this calculation.

1) The rates of sedimentation (w) used are 10^{-2} cms/yr and 10^{-1} cms/yr. These values are based on the sedimentation rate obtained by a geomagnetic method for sediment in the Inner sound closest to the mouth of Loch Alsh (Bishop, 1975) and on other studies on shallow coastal marine sediments (Chapter 3.8).

2) The diffusion coefficient (D_a) used in this calculation is 2.0×10^{-6} cm^2 sec^{-1} (Berner, 1971). This value is typical of the range of values used for ionic diffusion in sediments (Berner, 1971; Mannheim, 1970; Anikouchine, 1968) and compares with the value of 0.48×10^{-6} cm^2/sec for the diffusion coefficient of humic acids extracted from marsh soils measured at pH = 6 and I = 0.2M (Flaig and Beutelspacher, 1968). It is, however, noted that Duursma and Bosch (1970) found that the apparent value of the diffusion coefficient varied by a factor of up to 10^{-6} due to sorbtion processes within the sediment.

Measurement of the flux of excess Zn to the sediment surface

Assumed sedimentation rates (w) = 10^{-2} - 10^{-1} cms/yr

Dry sediment/pore water ratio at the surface (r) = 1/4

Surface enrichment of Zn = 67 µg/grm of sediment

Average density of sediment (d) = 2.6 grms/cms^3

Let no. of grms of sediment deposited/yr = S

$$S = w.\ d.\ r.$$

$S = 2.6 \times 0.25 \times (10^{-1} - 10^{-2})$ grms/cms^2/yr

$S = 0.65 \times (10^{-1} - 10^{-2})$ grms/cm^2/yr.

Let the flux of excess Zn to the sediment = F

$F = S \times$ conc. of excess Zn/grm of sediment

$F = 0.65 \times (10^{-1} - 10^{-2}) \times 67$ μgZn/cm^2/yr

$F = 44 \times (10^{-1} - 10^{-2})$ μgZn/cm^2/yr

$F = 1 \times (10^{-7} - 10^{-8})$ μgZn/cm^2/sec

Thus for $w = 10^{-1}$ cm/yr $F = 1 \times 10^{-7}$ μgZn/cm^2/sec

and for $w = 10^{-2}$ cm/yr $F = 1 \times 10^{-8}$ μgZn/cm^2/sec

Measurement of flux of DOC to sediment surface due to upward diffusion in the pore waters

Porosity of sediment (Φ) = 0.89

Conc. of HMW DOC at surface (C_0) = 7 mgC/ltr

Conc. of HMW DOC at 70 cms (C_{70}) = 55 mgC/ltr

Diffusion coefficient (D) = 2.0×10^{-6} cms/sec

Let the diffusive flux of DOC to the surface = J

Then $J = - \dfrac{D\Phi(C_{70} - C_0)}{h}$ (Berner, 1971)

This equation is valid if one considers the simple diffusion of HMW DOC between two reservoirs of constant composition with no reaction occurring between. Such a diffusion model would result in a form of DOC vs. depth graph similar to that which is found in the anoxic pore waters of Loch Duich (F1, A2 and A7).

$$J = - \frac{2 \times 0.89 \times 48 \times 10^{-6}}{70 \times 10^{3}} \text{ mgC/cm}^2\text{/sec}$$

$J = - 1 \times 10^{-9}$ mgC/cm^2/sec

For the upward diffusion of organically bound Zn to provide sufficient Zn to produce the observed trace metal enrichment, it is necessary that the concentration of organically bound (C) Zn (μg/mg DOC) is

for $w = 10^{-1}$ cms/yr $C = 100$ μgZn/mgDOC

for $w = 10^{-2}$ cms/yr $C = 10$ μgZn/mgDOC

or expressed as a percentage

C = 1.0 - 10.0% Zn/DOC

Note that although there is an increase in HMW DOM with depth, there is no systematic increase of Zn in the interstitial waters (Fig. 8.7). This results in the Zn/DOC ratio increasing with depth in the core, whereas one might expect that if the concentration of chelating agent (fulvic acid) were increased, then the concentration of bound Zn should increase as well. No explanation for this observation is given. However, this further suggests that a complex series of organic and inorganic interactions are occurring between the pore waters and the sediment.

Given the calculated flux of HMW DOC close to the sediment - water interface, a ratio of Zn to HMW DOC of 1 - 10% Zn/DOC is necessary to provide the observed trace metal enrichment.

Humic acids extracted from coastal marine sediments by base solubilisation followed by acid precipitation contained 0.2 - 0.5% Zn/DOC (Pillai et al., 1971). The HMW DOM, probably humic acid, separated from the pore waters of Saanich Inlet by dialysis contained 0.6% Zn/DOC. Both of these values of Zn/DOC are too low to provide sufficient Zn flux at the sediment surface. However, the HMW DOM

present in the pore waters of Loch Duich is mainly fulvic acid, which is a stronger chelator of trace metals than is humic acid (Desai et al., 1972). These authors show that fulvic acid extracted from marine sediments is able to solubilise up to 40 mgZn/grmFA (i.e. 8% Zn/DOC) of $Zn(OH)_2$ in a freshwater medium; humic acid can solubilise up to 1% Zn/DOC under similar conditions. It is thus shown from the limited data available that the Zn/DOC ratio in humic substances from other environments is of a similar magnitude to that required to explain the observed sediment enrichment of Zn.

The concentration of Zn in the HMW fraction as analysed directly in this study is too low to provide the necessary flux of dissolved Zn at the surface (0.1 - 0.3% Zn/DOC). However, the concentration of analysable Zn increases after oxidation. This is due to a release of strongly chelated Zn from organics (Chapter 8). Although there is significant concentration of organics in the LMW fraction, it is considered likely that most if not all the strong chelating agents are present in the HMW fraction, principally as fulvic acids. If this is valid, then the concentration of HMW Zn as analysed is too low, and the true concentration of Zn bound in the HMW fraction is better measured by the HMW concentration plus the increase in analysable Zn after oxidation (Table 9 III). The ratio of Zn/DOC at the surface calculated in this manner is 0.7 - 1.3%. This is in the correct range to provide a sufficient flux of Zn to explain completely the observed enrichment of Zn in the sediment, assuming that w = 0.01 - 0.03 cm/yr (Bishop, 1975) and that all the Zn/HMW DOM is removed at the sediment interface by biological or inorganic interaction.

In conclusion, it is possible to explain the observed surface

Table 9 III

Concentration of Zinc inferred to be present in the HMW fraction

Core and depth		Total concentration Zn		Δ Zn	HMW Zn	Δ Zn + HMW Zn	DOC	Zn/DOC %
		Irradiated	Untreated					
A2	5	600	423	177	43	220	16.8	1.3%
	15	155	98	57	15	72	22.4	0.3%
	25	128	70	58	23	81	25.2	0.3%
	35	96	33	63	26	89		
	45	78	10	68	2	70	38.4	0.2%
	55	60	16	44	8	52		
	65	117	47	70	38	108		
	75	89	27	62	10	72	55.9	0.1%
Average						96		
A7	5	537						
	15	156	25	131	12	143	24.2	0.6%
	25	153	19	134	19	153	29.4	0.5%
	35	214	18	196	8	204	34.6	0.6%
	45	47	35	12	16	28	42.2	0.06%
	55	131	26	105	13	118	43.6	0.3%
	65	132	45	87	22	109	48.5	0.2%
	75	77	189	-112	166	54	70.5	0.08%
	85	66	44	22	16	38		
Average						106		

enrichment of Zn and possibly Pb in the reducing sediments of the central basin of Loch Duich by a natural recycling mechanism in which the movement of these metals is controlled by the upward diffusive flux of dissolved "humic" substances which are produced within the sediment during diagenesis. The precipitation of these metals at the surface is probably controlled by biological action, principally the incorporation of the upward diffusing chelates into the body tissues and its incorporation into the sediment as faeces or on the death of the organism. Organic and inorganic absorption and oxidation processes may also be important. It is not, however, possible to conclude that this is the only source of this surface excess, since it is known, particularly in the case of Pb that there is an anthropogenic flux present. In the sediments of Loch Duich it is considered likely that this is only a minor component.

Such a diagenetic mechanism for trace metal enrichment is able to explain the observations that

1) Pb and Zn are the only two elements consistently showing enrichment in all the areas considered, whether a local source of pollution is present or not.

2) The absolute concentrations of trace metal enrichment are similar in areas of "high" anthropogenic flux such as in the California borderlands (Bruland et al., 1974) and Byfjord (Ollausson, 1975) and also in areas where there is no obvious local source of pollution, West Norway (Taylor, 1974) and N.W. Scotland (Price, 1973; this paper).

3) There is a significant difference between the sedimentation rate necessary to explain the observed surface enrichment in the basin

sediments of Loch Duich if no diagenetic redistribution has occurred ($\sim$1 cm/yr) and the inferred sedimentation rate of (10^{-1} - 10^{-2} cm/yr).

In considering surface trace metal enrichment in recent sediments care must be taken to avoid taking a simplistic view, and if possible an attempt must be made to differentiate between the natural diagenetic recycling process and recent anthropogenic input, since both will result in an enrichment of trace metals in the surface few centimetres of the sediment.

CHAPTER 10

SUMMARY

The purpose of this study was to examine the reactions and interactions of trace metals and organic matter in recent marine sediments. In order to do this an integrated study of the geochemistry of the sea water, sediments and their interstitial waters, of Loch Duich was performed. The results are related as far as possible to metabolic processes and diagenetic reactions which are occurring within the sediment. Loch Duich was chosen for this study because it is (1) in a relatively unpolluted region of Britain and thus changes in sediment chemistry can be related to natural diagenetic changes, (2) it contains in close proximity highly reducing and oxic sediments and (3) the sediments remain lithologically homogeneous within a single core and thus any geochemical trends observed can be interpreted in terms of diagenetic changes or variations in sediment flux.

Loch Duich has a typical fjord type estuarine circulation with three layers, a thin (5 - 10 metres) surface layer of brackish water flowing outwards from the rivers, a middle layer (10 - 60 metres) which contains water of a characteristically higher salinity than the water above and below, which is the water mass that flows in over the sill and a lower (60 - 120 metres) layer of colder saline water. Because of the large tidal range (5 metres), the waters in Loch Duich are well mixed and remain oxic throughout the year.

The analysis of the geochemistry of suspended particulate matter in the water column shows a linear correlation between Ti and Al and an

irregular increase in both from the surface waters to the bottom due to resuspension of sediment throughout the water column. The surface layers 0 - 20 m have a large excess of Si and P over Al which is due to biogenic production (mainly plankton). Below the surface the Si and P levels remain relatively constant. The Si/P ratio increases with depth, suggesting that P is more rapidly recycled within the water column than Si, probably because Si is mainly present within the skeletal material of the organisms.

The Fe/Al ratio shows that Fe is present mainly in the detrital phase except for the surface and bottommost samples which show a small but significant excess of iron (approximately 10%). The surface excess is interpreted as fresh water humic acids rich in iron which have flocculated at the sea water/fresh water interface and which have then been carried out within the surface brackish water layer. Such an interpretation is consistent with the observations made on particulate matter from the surface waters of Loch Etive (Price and Calvert, 1973) and laboratory flocculation experiments (Sholkovitz, 1976). The excess particulate Fe in the bottom waters is evidence of the presence of a thin oxic layer to the sediment rich in Fe and Mn oxides.

The particulate matter and the underlying sediments have a similar P/Al and Fe/Al ratio, but the particulate matter in the water column has a lower Ti/Al ratio due to a finer grain size of the detritus in the water column and a higher Si/Al ratio due to the presence of a large quantity of broken diatom frustules.

Two sediment types were sampled in the Loch Duich basin, a central basin sediment which was characteristically a black fetid mud and an oxic muddy sand from Loch Beg.

The mineralogy, grain size, major and trace element geochemistry were compared for sediments from these two localities. It was concluded that the sediments and organic matter in Loch Beg are principally of terrestrial origin, while in contrast the sediments of the Loch Duich basin are characteristic of a well degraded organic rich marine sediment.

Three biogeochemical zones, oxic, sulphate reducing and methane producing were recognised within the sediments of Loch Duich. These zones are identified by the characteristic concentrations of certain anions (PO_4^{3-}, NH_4^+, HCO_3^-, SO_4^{2-} and S^{2-}) and control the physico-chemical conditions within the sediment interstitial waters. They represent a series of metabolic reactions for the conversion of organic matter to energy using O_2, SO_4^{2-} and CO_2 as the oxidant respectively. This sequence of biogeochemical zones has been recognised in a series of different marine sediments (Claypool and Kaplan, 1974).

The oxic zone has characteristically similar concentrations of nutrient anions to sea water, no free sulphide and little or no enrichment of HMW DOM (yellow colour). The sulphate reducing zone has an increasing accumulation of nutrients (HCO_3^-, PO_4^{3-}, NH_4^+), an exponential decrease in SO_4^{2-} from sea water values to zero and an increasing accumulation of sulphide. The increase in sulphide (0 $\longrightarrow$ 2 mM/l) is less than the decrease in sulphate (27 mM/l $\longrightarrow$ 0) from which the sulphide is derived due to the formation of metal sulphides, principally Fe sulphides, within the sediment. There is also an increasing yellow colour of the pore waters due to the accumulation of DOM. Typically, the methane producing zone has a continued accumulation of HCO_3^-, NH_4^+ and PO_4^{3-} and DOM, though often at a somewhat different rate. Since

no more sulphide is being produced, the concentration of sulphide in the water decreases due to incorporation into the sediment.

A series of experiments was performed to investigate the use of light absorbance as a measure of total DOC. It was shown by calibration against DOC (measured by total dry combustion) that absorbance at 280 nm and natural pH (7 - 8) was a very accurate and simple measure of the total DOC in pore waters.

The total DOC in the sediment interstitial waters remains approximately constant in the oxic zone 10 - 16 mgC/ltr and then accumulates throughout the anoxic zones 12 ⟶ 70 mgC/ltr with no significant change in the rate of accumulation of DOC between the sulphate reducing and methane producing zones. This is interpreted as being experimental confirmation that a third anaerobic metabolic process is occurring, a type of fermentation process. Claypool and Kaplan (1974) suggest that such a process has to occur in order to provide the LMW organics required as a substrate by sulphate reducing bacteria.

Additionally, the pore waters were ultrafiltered using an Amicon UM-2 ultrafilter with a molecular weight exclusion limit of 1000. Measurement of the DOC concentration of the HMW retained fraction and the LMW ultrafiltrate showed that the increase in total DOC in the anoxic pore waters from 12 ⟶ 70 mgC/ltr was entirely an increase in HMW organics, the LMW organics remaining constant at approximately 10 mgC/ltr throughout the three biogeochemical zones. These results confirm the conclusion of Nissenbaum and Kaplan (1972) that the humic acid found in recent marine sediments is principally autochthonous.

The UV continuous spectrum and the spectral ratio of light absorbances at 320/420 nm (E_3/E_4) and at 420/620 nm (E_4/E_6) were investi-

gated as well as the IR spectrum of the acid insoluble precipitate. The continuous spectrum is similar to that found for marine derived humic substances (Kalle, 1961; Nissenbaum et al., 1971) and shows that a considerable fraction if not all the HMW DOM is humic in nature. A quantitative analysis of the E_4/E_6 ratio, 6.75 - 17.0 is interpreted as being due mainly to the presence of fulvic acids and another phase which has a high E_4/E_6 ratio. This second phase is thought to be similar to the algal exudate investigated by Sieburth and Jensen (1968 a,b) and Ogura and Hanya (1972a,b) and probably chemically analogous to melanoidin, a condensation product of carbohydrates and amino acids (Kalle, 1966; Manskaya and Drozdova, 1968). In addition, an IR spectrum of the precipitate when pore water samples are acidified was identified as being characteristic of humic substances (Nissenbaum et al., 1971) and probably humic acid sensu stricto. This humic acid represents only a small fraction ($\sim$1%) of the total HMW DOM, the remainder being fulvic acid and algal exudate (melanoidin) with an increasing proportion of algal exudate (melanoidin) relative to fulvic acid down the core corresponding to an increase in spectral ratio.

This work suggests that this HMW material represents an intermediate stage in the conversion of dead cellular material $\longrightarrow$ LMW organic matter (such as amino acids, carbohydrates, porphyrins and fatty acids) $\longrightarrow$ HMW organic matter (such as humic acid, fulvic acid and melanoidins) $\longrightarrow$ humic substances in the sediment and ultimately humins.

Total organic carbon, total nitrogen and total phosphorus in the sediment show no discernible diagenetic trend in any of the cores considered. There are, however, significant increases in C/N and C/P in the anoxic core and also C/N in the oxic cores, showing a

preferential loss of N and P relative to C during diagenesis. It is, however, not possible to relate changes in C, N and P in the sediment directly to the accumulation of anions in the pore waters. It is calculated that the accumulation of anions in the pore waters, neglecting diffusion and advection, represents a relative change of approximately 1% TOC, 0.5% TN and 1% TP. Thus although the concept of metabolisable organic matter which decomposes in a first order reaction to release anions to the pore is interesting, in practice it does not appear to be measurable for C, N and P in sediments.

I and I/C show a diagenetic decrease in both oxic and particularly anoxic cores. This decrease is shown to be first order with respect to iodine concentration assuming a uniform rate of sedimentation, and thus if a value for accumulating pore water iodine could be obtained, a calculation similar to those used by Berner (1974) relating pore water accumulation directly to organic matter breakdown could be performed.

The observed geochemistry of iodine in the top metre of anoxic sediments can be explained by a recycling mechanism in which the organic matter in the upper five centimetres of the sediment becomes enriched in I due to microbial and inorganic absorption. This organic matter is buried and becomes solubilised by metabolic decomposition. This dissolved I phase then diffuses back up to the surface to be absorbed and recycled.

It is known from this and previous studies on sediment interstitial waters that trace metals are often enriched by an order of magnitude or more over their concentration in the overlying sea water due to diagenetic reactions occurring within the sediment. The

solubility of Cu, Zn and Fe in the presence of 1 mMole/l of free sulphide is several orders of magnitude less than that found in sediment pore waters and it is suggested that this increased solubility might be due to the presence of trace metal organic chelates (Brooks et al., 1968). Additionally, it is known that trace metal - organic chelates exist in sea water, and thus, since the concentration of organic matter in pore waters is higher than that in sea water, such chelates are likely to exist and possibly be important in controlling the solubility of trace metals in anoxic pore waters.

The results of the analysis of total dissolved trace metals show that Mn behaves in a significantly different manner to Fe, Cu and Zn. Mn shows a large surface enrichment in those cores with the oxic - anoxic redox boundary close to the sediment - water interface, of 727 - 13,500 ppb which decreases to a value of 39 - 56 ppb at a depth of 65 centimetres. This surface enrichment is not present in the oxic cores, which remain relatively constant through their length with similar concentrations to those found in the anoxic cores (15 - 87 ppb).

The profiles of Fe and Cu show no systematic trend with depth with average values for Fe being 61, 67 and 84 ppb in the anoxic cores and slightly lower values, 27 and 50 ppb, in the oxic cores, while Cu gives average values of 19, 17 and 6 ppb in the anoxic cores and 8 and 9 ppb in the oxic cores. Zn appears to vary systematically with depth , with cores F1 (62 ← 15 ppb) and A2 (423 - 98 ← 27 ppb) showing a decrease, core A7 (25 → 44 - 189 ppb) showing an increase and core A3 showing no systematic trend. No explanation for this behaviour of Zn is given. All of these concentrations for

both oxic and anoxic cores are an order of magnitude at least greater than the measured concentration in dissolved trace metals in the overlying water column, Mn 0.7 - 4.4 ppb, Fe 0.9 - 8.5 ppb, Zn 1.4 - 8.2 ppb and Cu 0.3 - 3.3 ppb.

Mn is present in the pore waters mainly in the LMW fraction and shows no significant increase in concentration after oxidation. In addition, MnS is relatively soluble compared to CuS, ZnS and FeS and Mn is the least likely of these elements to form organic chelates (Irving and Williams, 1948). It is thus concluded that Mn is mainly present as labile inorganic complexes.

The solubility of Mn is controlled indirectly by the decomposition of organic matter. In those cores where the oxic - anoxic redox boundary is close to the sediment - water interface, there is a surface enrichment of up to 2 ppm relative to a background level of 50 ppb in the oxic cores and at depth in the anoxic cores. There is an exponential decrease in Mn concentration with depth in the anoxic cores. Assuming steady state conditions, the increase in concentration of Mn immediately below the oxic - anoxic redox boundary is due to the solution of solid Mn(IV) oxide and hydroxide phases as Mn(II) after burial. The dissolved Mn(II) then diffuses upwards to be precipitated and redeposited as Mn(IV) phases or diffuses downwards. In order to maintain the observed Mn(II) excess close to the sediment surface, two possible mechanisms are suggested:

1) vertical advection exactly balances downward diffusion (Taylor, 1974) , or

2) there is a steady state removal of Mn as manganous carbonate phases at depth within the sediment (Calvert and Price, 1972).

Saturation calculations showed that the pore waters of anoxic sediments in Loch Duich are saturated or supersaturated with respect to manganous carbonate and thus the reduction of dissolved Mn with depth is probably due to its removal as a disseminated manganous carbonate phase within the sediment. The control on the solubility of Mn at depth within the core is bicarbonate anions which are produced during sulphate reduction in the pore waters. This is a similar mechanism to that suggested to explain the Mn distribution in Loch Fyne (Calvert and Price, 1972) and the Arctic basin (Li et al., 1969). The total overall concentration of Mn is much lower in Loch Duich than in Loch Fyne and the Arctic basin, and thus it is inferred that this mechanism for Mn diagenesis is valid both in coastal regions with a concentration of Mn sufficient to result in the formation of an identifiable $MnCO_3$ phase and in regions with much lower concentrations of Mn, such as Loch Duich.

Fe, Zn and Cu showed no simple trend with depth and specifically it was not possible to relate the concentration of these metals to observed changes in sulphide, pE or total DOC. From this it was inferred that these metals could not be present as labile complexes, since such complexes would be affected by changes in the geochemistry and particularly would be precipitated as trace metal sulphides. The observation that the trace metals do not show a simple correlation with total DOC does not mean that all the trace metals could not be bound to organics, because it is known both from this study and previous work that certain fractions of the dissolved organic matter are much more important in associating with trace metals (i.e. humics) than are other fractions (hydrocarbons, amino acids) which have also

been detected in anoxic pore waters. Thus total DOC is unlikely to be a good measure of the presence and concentration of organic chelates.

Results presented in this study show that a large proportion of Fe, Cu and Zn in the pore waters of reducing sediments are bound to organic chelates. The evidence for this conclusion is:

1) A comparison of the concentration of trace metals in anoxic pore waters before and after oxidation shows that 45 - 69% of the Fe and 16 - 70% of the Zn is organically bound. This is a minimum value (Kamps-Nielsen, 1972).

2) The presence of Cu (61 - 66%), Fe (56 - 77%) and Zn (27 - 58%) in the HMW fraction coincident with a high concentration of humic type organic matter which is known to be a strong trace metal chelator.

3) The fraction of Cu, Fe and Zn in the HMW fractions is considerably reduced from 17 - 66% 6 - 26%, 48 - 77% 22 - 44% and 12 - 58% 11 - 18% after oxidation, which results in the complete removal of DOC from the pore waters and specifically the breakdown of "humics".

4) The presence of 8 - 20% of the total dissolved Fe in the acid insoluble humic acid precipitate. This precipitate is spectroscopically similar to the dialysed material separated from the pore waters of Saanich Inlet sediments and contains a similar concentration of Fe (0.3% by weight of the precipitate). The Saanich Inlet organic matter also contained a significant concentration of Zn and Cu, which was thought to be removed from the humic acid precipitate of the Loch Duich pore waters by acid treatment.

It was concluded that the Cu, Fe and Zn in the HMW fraction of the pore waters was present mainly as organic "humic" chelates,

although some other organic chelates and complexes are possible as well as some inorganic colloidal and particulate matter. The trace metals in the LMW fraction are not labile inorganic complexes, but bound as either LMW organic chelates such as porphyrins or possibly as polysulphides.

Trace metals were analysed in the sediment by XRF. Rb remained constant within each core, confirming their lithological homogeneity. Fe and Mn also showed no trend with depth, though it is suggested that an Fe/Mn rich oxide phase may be present at the surface which was not sampled by the coring technique used. There was a surface excess of Pb of 38 - 57 ppm ← 26 - 28 ppm at 75 cms and a surface excess of Zn of 150 ppm ← 90 ppm at a depth of 75 cms in the anoxic cores, while a lesser enrichment 33 - 47 ppm ← 34 ppm (Pb) and 115 ← 79 ppm (Zn) was observed in the oxic cores. The values obtained for Cu were somewhat erratic, and there was no surface enrichment for Ni.

The surface enrichment of Pb and Zn is entirely present in the non-lithogenous phase, while substantial proportions of Fe (30%), Mn (65%) and Cu (60%) are also present in this phase. Although all the enrichment is present in the non-lithogenous phase, there is no simple correlation with TOC or with Fe and Mn metals which are usually taken as a measure of the oxide/sulphide phases which might be expected to coprecipitate trace metals in sediments.

The surface enrichment could be due to a recent anthropogenic flux of Pb and Zn or to a natural diagenetic recycling mechanism or to a combination of both processes. The trace metal enrichments are compared and contrasted with similar enrichments observed in areas

with no local source of pollution; Loch Fyne (Price, 1973), Mofjord and Bolstadfjord (Taylor, 1974), Saanich Inlet (Presley et al., 1972) and areas adjacent to major centres of population, Byfjord (Olaussen, 1975), the Baltic Sea (Erlenkeuser et al., 1974) and several basins from the California borderlands (Bruland et al., 1974).

It is to be noted that the Baltic sea samples show a significantly greater surface enrichment of Cu, Zn and Pb than do any of the other samples either from "polluted" or "unpolluted" areas. The remaining sediments give Pb, Zn and Cu enrichments of similar orders of magnitude.

If the principal cause of the surface trace metal enrichment in Loch Duich and elsewhere is due to pollution, it is necessary to explain

1) The trace metal enrichments for Pb, Zn and Cu found in the "polluted" sediments of California and Byfjord are similar in magnitude to those found in the "unpolluted" fjords of Norway and Scotland.
2) The only sources of pollution likely to affect Loch Duich are regional fluxes which should result in regional trends of trace metal distribution.with the anthropogenic flux decreasing with the square of the distance from its source.
3) The surface excess in the sediments is shown most clearly in Pb and Zn while the air borne particulate matter shows an excess of Pb and Cu and no excess of Zn.

A natural diagenetic recycling method is suggested which depends on the diffusional migration of organically bound trace metals and could explain the surface excess of Pb and Zn (and the absence of an excess for Fe) independent of any anthropogenic flux. Trace

metals present in the sediment input become buried. Organic matter, particularly humics which are released into the pore waters during diagenesis, solubilises these trace metals; this results in an upward diffusive flux of trace metal - organic chelates. These chelates are removed from solution close to the sediment surface by metabolic absorption by benthos and removal as faeces, by incorporation into bacteria which are fixed to inorganic particles or by inorganic oxidation in those situations when the oxic - anoxic redox boundary coincides with the sediment - water interface.

A calculation is performed which demonstrates that upward diffusing pore waters could provide the necessary flux of trace metals for the observed Zn enrichment. It is thus concluded that a natural diagenetic process is a possible mechanism to explain the observed trace metal enrichments and that it is not possible to consider Pb and Zn enrichment in recent sediments even in areas of obvious local pollution as being necessarily entirely due to anthropogenic inputs.

A P P E N D I X A

Shipboard measurements and sample collection

1) Salinity and temperature determinations

Salinity and temperature were measured in situ with an N.I.O. portable Salinity-Temperature Bridge (Type M.C.5). The salinity and temperature readings were calibrated against Standard Copenhagen Sea-water (S^{o}/oo = 35.00) and a laboratory Hg thermometer respectively. The estimated precision* for temperature and salinity are $\pm$ 0.2^{o}C and $\pm$ 0.1$^{o}/oo$ respectively.

2) Water sampling

Four 7 litre N.I.O. polyvinyl chloride/nylon water bottles were used to sample water. Immediately on retrieval of a bottle, two subsamples were collected. For this purpose a plastic tubing extension was fitted over the bottom tap of the bottle. Subsampling was as follows:

a) an 'oxygen' bottle ($\sim$300 mls) was filled until overflowing, care being taken to avoid the inclusion of any air bubbles. The subsample was immediately pickled with 3 mls $MnCl_2$ solution and 3 mls of NaOH/NaI solution, after which the bottle was stoppered. Analysis

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* Precision here is expressed as the coefficient of variation (V_x)

$$V_x = \frac{\sigma_x}{\bar{x}} \cdot 100\%$$

where σ_x is the standard deviation and $\bar{x}$ is the sample mean.

for dissolved oxygen was performed in the laboratory in Edinburgh within four days.

b) the remainder was collected in acid-cleaned 5 litre polythene jerry cans following a single rinse of the water sample. These cans of water were transported back to the laboratory in Edinburgh where they were filtered within four days. A 500 mls subsample was thoroughly shaken and then vacuum filtered through 0.45 u Nucleopore filters (47 mm diameter). The material remaining on the filters was stored in a dessicator at 5°C until it could be analysed for the major elements in this suspended particulate matter by an X-ray fluorescence method. The remaining seawater was vacuum filtered through 0.45 u SARTORIUS membrane filters (composed of Cellulose nitrate), the filtered seawater returned to the jerrycan and stored at 5°C until required for trace metal analysis.

3) Coring

A 1.5 m stainless steel gravity corer with transparent plastic core liner (4 inches in diameter) and an aluminium "fingers-type" core catcher was used to sample sediments in April 1974. In February 1975 an improved gravity corer designed by E.R. Sholkovitz was used to sample the sediment. This corer has no stainless steel outer tube, core cutter or aluminium core catcher, instead the sediment is held in the unsupported core liner by a vacuum seal at the top of the tube. This results in a less disturbed sediment and less chance of metal contamination.

Immediately on retrieval of the coring device, the transparent core liner was removed and the core length and general lithology of

the sediment were noted. The core liner was sealed at both ends with plastic caps and most of the water overlying the sediment was drained off by boring a hole through the liner a few centimetres above the sediment surface. The core was then stored upright at ambient temperature (0 - 10^{o}C). All the cores were transported back to Edinburgh by road within 36 hours of collection and then stored upright at 5^{o}C for a maximum of 48 hours until the pore waters could be extracted from the sediment.

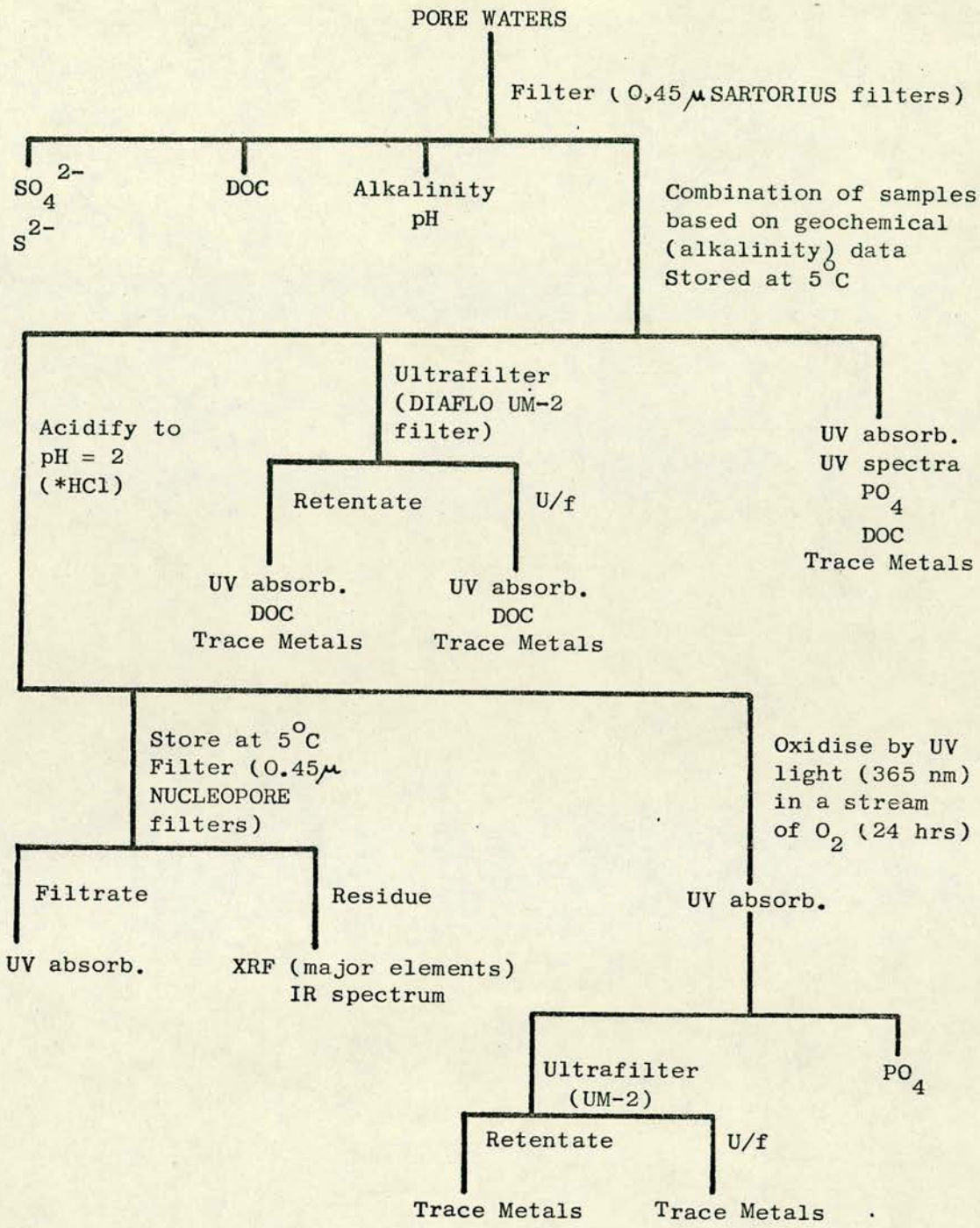


Fig. B.1; Flow diagram showing the scheme of analysis of the sediment interstitial waters.

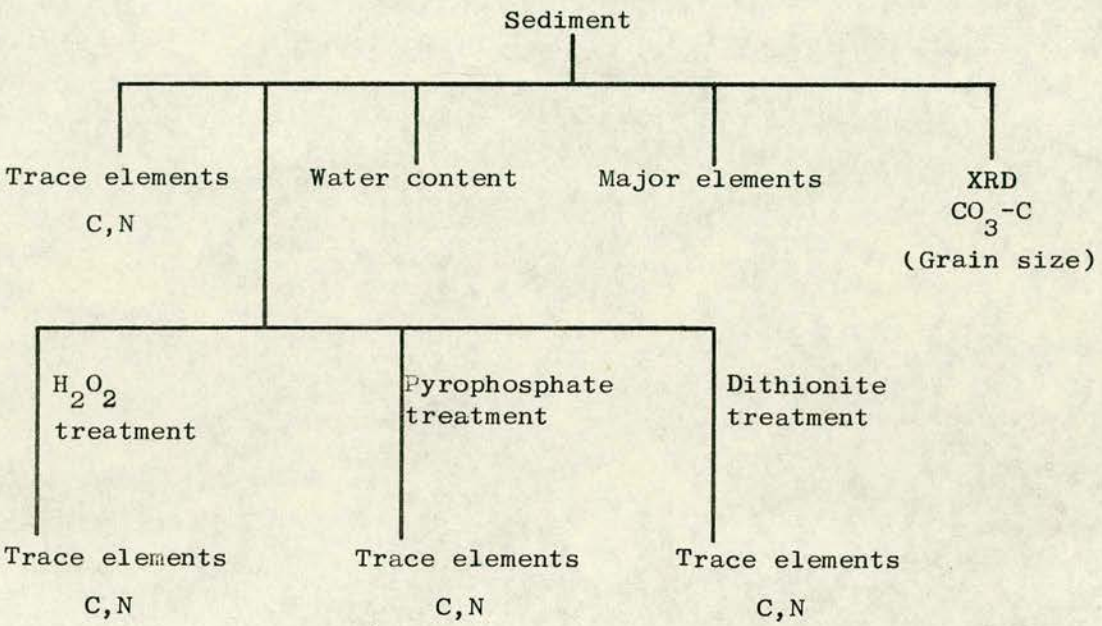
DOC is the analysis of carbon by dry combustion.

UV absorb. is the measurement of light absorbance at fixed wavelengths.

UV spectra is the measurement of a continuous light spectrum.

Fig. B 2

Flow diagram showing the scheme of analysis for the sediment



Trace elements and major elements were analysed by X-ray fluorescence.

APPENDIX B

Storage, sampling, treatment and analysis of samples in the laboratory

Figure B.1 represents a flow diagram for the analysis of pore waters in the sediment and Figure B.2 shows the reaction scheme for the analysis of the geochemistry of the sediment after the extraction of the pore waters.

Extraction of pore waters from the sediment

A low pressure mechanical squeezer was used to extract the pore waters from the sediment with the minimum of air contact. The apparatus used was based on that of Kalil and Goldhaber (1973) with certain minor modifications. The core was cut into 10 cms lengths using a hacksaw. One centimetre of sediment from each end was discarded to enable the nylon end-pieces to be fitted and also to minimise possible metal contamination. A subsample of this discarded sediment was used for water content determinations (Table B I). The sediment was squeezed for up to $1\frac{1}{2}$ hours until little further pore water could be extracted and the core liner was showing severe bulging. The first 10 - 15 mls of pore waters was discarded (Troup et al., 1974) and the remaining waters collected in acid cleaned polythene bottles. The pore waters were then vacuum filtered through 0.45 μ Sartorius filters and then immediately subsampled for later analysis of DOC, sulphide and alkalinity. In April 1974 two subsamples were taken; 5 mls was pipetted into a glass jar for alkalinity determinations and 10 mls into a plastic bottle which contained a few crystals

Table B I

Water content of sediment

Core and depth (cms)		wet/dry (x100%)	wet/total (x100%)	Core and depth (cms)		wet/dry (x100%)	wet/total (x100%)
F1A	0	279.7	73.67	F1B	0	304.53	75.28
	10	220.9	68.84		10	244.89	71.00
	20	279.3	73.64		20	254.61	71.80
	20	205.6	67.27		20	233.94	70.05
	30	204.2	67.13		30	210.04	67.75
	30	201.8	66.87		30	207.32	67.46
	40	181.8	64.45		40	224.38	69.17
	40	174.2	63.53		40	198.10	66.45
	50	174.2	63.53		50	177.79	64.00
	50	168.7	62.78		50	192.77	65.84
	60	191.6	65.71		60	185.71	65.00
	60	187.9	65.26		60	182.75	64.63
	70	166.3	62.45		70	173.12	63.39
	70	196.5	66.27		70	176.23	63.80
	79	204.2	67.13		80	189.80	65.49
	79	199.2	66.57		80	260.07	72.23
	88	187.0	65.15				
F4A	0			F4B	0	250.76	71.49
	10	182.49			10	161.68	61.78
	20	170.16			20	159.62	61.48
	20	138.14			20	124.64	55.48
	30	135.58			30	127.97	56.13
	30	143.64			30	138.35	58.04
	40	140.6			40	140.72	58.46
					40	145.60	59.28
A2	0	210.86	67.83	A7A	0	241.31	70.7
	10	205.03	67.22		10	200.0	66.67
	20	186.32	65.07		20	183.06	64.67
	30	162.45	61.90		30		
	40	167.25	62.58		40	183.25	64.70
	50	188.04	65.28		50	206.30	67.35
	60	168.36	62.74		60	198.68	66.52
	70	180.34	64.33		70	197.61	66.40
A3A	0	208.41	67.58		80	182.65	64.60
	10	220.0	68.75		90	189.96	65.51
	20	223.14	69.05				
	30	228.27	69.54				
	40	202.5	66.94				
	50	201.94	66.88				
	60	192.67	65.83				
	70	162.75	61.94				

Table B Ia

Water content of sediment before and after the extraction of pore waters

Before extraction				After extraction		
Core and depth (cms)		wet/dry (x100%)	wet/total (x100%)	Core and depth (cms)	wet/dry (x100%)	wet/total (x100%)
F1C	0	290.36	74.38	0	63.74	38.93
	10	177.12	63.91	15	71.88	41.82
	20	170.16	62.98	25	65.62	39.62
	20	204.73	67.18			
	30	194.18	66.01	35	74.45	42.68
	30	204.75	67.19			
	40	196.16	66.23	45	70.37	41.30
	40	193.03	65.87			
	50	181.37	64.46	55	57.52	36.52
	50	172.59	63.32			
	60	178.88	64.14	65	80.91	44.73
	60	151.97	60.31			
	70	154.97	60.78	75	93.69	48.37
	70	189.27	65.43			
	80	193.14	65.89			
	88	191.56	65.70			
A4A	0	138.97	58.15	5	56.75	36.2
	10	138.72	58.11	15	43.09	30.12
	20	104.33	51.06	25	44.15	30.63
	30	119.27	54.39	35	49.32	33.03
	40	148.83	59.81	45	140.90	58.49
	50	201.43	66.82	55	52.99	34.63
	60	155.70	60.89	65	55.09	35.52
	70	178.6	64.11	75	45.48	31.26
A7B	0	264.02	72.53	5	83.16	45.40
	10	211.63	67.91	15	61.71	38.16
	20	192.71	65.84	25	76.18	43.21
	30	239.9	70.58	35	76.26	43.27
	40	175.27	63.67	45	94.77	48.66
	50	213.41	68.09	55	58.90	37.07
	60	203.6	67.06	65	72.19	41.92
	70	210.13	67.76	75	63.0	38.65
	80	205.54	67.27			

of cadmium nitrate for sulphide determination. In February 1975 these two subsamples were taken plus a further 15 mls sample of pore water which was pipetted into an acid cleaned glass jar for determination of DOC by the dry combustion method.

This method of sediment squeezing for the extraction of pore waters resulted in the removal of approximately 50% of the total interstitial waters, the water content being reduced from 60 - 75% of the total sediment to 30 - 50% (Table B Ia). This represents typical values for the water content of a compacted sedimentary rock (Pettijohn, 1957) and are thus the maximum value for removal of interstitial waters possible by a mechanical method of extraction. Note that the term pore waters or interstitial waters used throughout this study refers to the extractable waters, no information is available on the chemistry of the residual pore waters which are in direct contact with the sediment particles.

The pore water geochemistry of sediment sampled from the same locality on successive trips using this squeezing technique was compared to interstitial waters extracted by a method of centrifugation (Davies, 1976). The concentrations of sulphate and titration alkalinity (Fig. B.3) were similar, however the measured concentrations of dissolved sulphide are greater often by an order of magnitude for the samples extracted using the mechanical squeezing technique.

Sampling of sediment

The sediment was removed from the squeezer as a hard tablet and a representative subsample removed for sediment analysis. The subsample was placed in a glass jar and dried for 36 hours at 75^{o}C

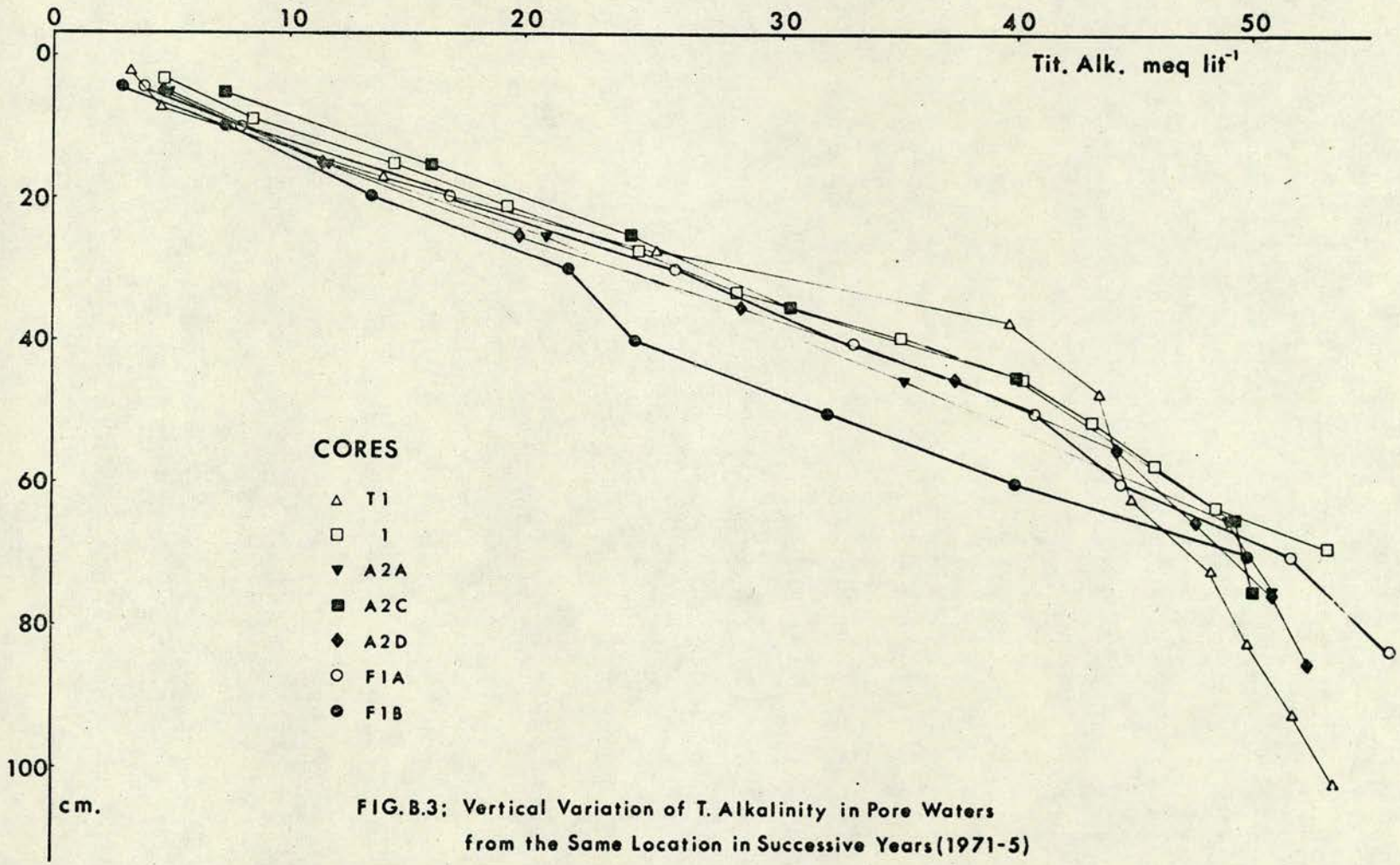


FIG. B.3; Vertical Variation of T. Alkalinity in Pore Waters from the Same Location in Successive Years (1971-5)

(April 1974) or for 48 hours at $\sim 50^{o}C$ (February 1975) and then ground (homogenised) to a fine powder using a tungsten carbide TEMA disc mill. The dried and ground sediment was then stored until required for analysis and chemical treatment.

Analysis of interstitial waters

Determination of titration alkalinity

Titration alkalinity was determined using the potentiometric method of Edmond (1970) and the results processed by the method of Gran (1952). The precision of the method was determined by a set of 9 replicate analysis on a sea water sample and found to be $\pm$ 1.4% (S.D. x 2).

Figure B.3 represents the titration alkalinity in the pore waters of a series of cores collected from the same location in the same year and in successive years. All the alkalinity results show a close correspondence both in intercept and gradient. For a single value of alkalinity there is a spread of $\pm$ 1 cm for the depth of core sampled. It is concluded from these results that it is a valid procedure to resample a single location in successive years and compare the results directly.

In addition, within the errors of analysis, the pore water geochemistry of the major anions behave as a steady state (sampled over a 4 year period) 1-dimensional (the accuracy of locating the coring station is only $\pm$ 50 m) system. The spread of data is interpreted as being due to the loss of differential amounts of the top of the core by a splash effect during the coring process.

Each 10 cms length of core provided $\sim$ 60 - 120 mls of pore

water for analysis. This volume was insufficient for the series of experiments that were to be performed on each pore water sample. The pore waters from two or more cores collected from the same location were combined using geochemical (alkalinity) criteria; samples with the most similar value of alkalinity were mixed. The method of combination is set out in detail in Chapter 8.2.

Sulphide

The concentration of dissolved sulphide in the pore waters was determined by means of an iodine/thiosulphate titration method. A 10 mls subsample was pipetted immediately after collection onto about 25 mg cadmium nitrate which fixed the sulphide as CdS. During the analysis, hydrogen sulphide was liberated by acid in the presence of a standardised iodine solution, some of the iodine forms iodide and the excess was titrated with standard sodium thiosulphate. Iodate was used as the primary standard.

Sulphate

Sulphate was determined on the samples previously used for sulphide determinations. Sulphate was precipitated as barium sulphate and measured gravimetrically.

Phosphate

The method used is a slight adaptation of that for reactive phosphorus in Strickland and Parsons (1968). A phosphomolybdate complex was reduced by ascorbic acid to a blue colour and then measured spectrophotometrically at 885 nm. The method is standardised against a solution of potassium dihydrogen phosphate.

Measurement of dissolved organic carbon

UV spectroscopy

Subsamples of untreated pore waters were measured for UV absorption in 1 cm quartz glass cells using a UNICAM SP 1800 spectrophotometer. The readings were measured against a filtered sea water blank and the instrument calibrated using a single pore water sample (A2C40) to ensure that results obtained on different occasions were directly comparable. The absorption was expressed both in the form of a continuous spectrum (fast scan rate) and as the specific absorbance at a series of wavelengths (240, 280, 320, 420 and 620 nm). The specific absorbance was used as a measure of DOC (see Chapter 6) and also in order to calculate the two spectral ratios E_3/E_4 and E_4/E_6 used in this study.

Determination of DOC by dry combustion

A dry combustion method for the analysis of DOC in pore waters based on the method of Gordon and Sutcliffe (1973) was used. This method involves the analysis of a 0.1 grm sample of dried pore waters in a PERKIN ELMER 240 C-N elemental analyser.

A 15 mls subsample of pore water was pipetted into an acid-cleaned glass jar immediately after squeezing. 0.1 ml of aristar syrupy H_3PO_4 was added and the sample placed in a dessicated oven at 30°C for 72 hours until the water had completely evaporated. The dry salt sample was then stored in a dessicator until ready for analysis, it is important that the sample is as dry as possible before it is presented to the C-N analyser. Approximately 0.1 gram of dried salt was weighed out accurately into a small silica boat and presented to the C-N analyser for combustion at 720°C in a stream of

O_2. The C-N analyser was calibrated every day using acetanalide and also occasionally using cellulose and urea, two compounds known to be highly resistant to analysis by conventional wet oxidation techniques (Williams, 1969). In addition, every sample was run in duplicate and if the two results differed by more than ~10%, the error claimed by Gordon and Sutcliffe (1973) for the analysis of DOC in seawater, then further analyses were performed to obtain a mean value.

Dissolved trace metals in interstitial waters

A method involving a chelate extraction and atomic absorption spectrometry (A.A.S.) was used to determine the concentration of dissolved Mn, Fe, Zn and Cu (Duchart et al., 1973; Taylor, 1974). The trace metals were extracted by sodium diethyldithiocarbamate (NaDEDTC) into 4 methylpentan-2-one (MIBK). The MIBK with DEDTC - metal complex was then aspired into an air-acetylene flame of the AAS.

4 x 15 mls portions of each interstitial water sample were transferred into 100 ml separating funnels. Aliquots of 0, 0.1, 0.2 and 0.3 mls of a mixed metal standard solution were added to these subsamples. The pH was accurately adjusted to 2 using 2N aristar HCl, this step was to ensure that the metals remain in solution. 0.5 mls of freshly prepared 2% $NH_2OH.HCl$ was added to ensure that Fe and Mn remained in solution after the pH was lowered. After a few minutes the pH was accurately adjusted to 6 with 2N aristar ammonium hydroxide. A 10% solution of sodium diethyldithiocarbamate (NaDEDTC) was prepared. A few mls of Analar grade 4 methylpentan-2-one (MIBK) were added to the NaDEDTC, placed in a separating funnel, and the whole shaken. The aqueous layer was run off and the

MIBK layer discarded. This extraction procedure was repeated twice. 5 mls of the purified aqueous solution of NaDEDTC was added to each of the separating funnels followed by 10 mls of MIBK and the funnel transferred to a mechanical shaker. The funnels were shaken for 30 minutes. After shaking the funnels were replaced on their stands and allowed to settle for five minutes. The aqueous layer was run off and discarded, the MIBK layer was collected for analysis in quick-fit test tubes. The metal content of the organic solutions was determined with a VARIAN-TECHTRON AA4/5 atomic absorption spectrometer, Mn was always the first metal determined.

A complete blank was performed each day for each set of 3 analyses using a 15 ml sample of freshly distilled and deionised water instead of the pore water sample. In general the blank for Mn and Fe was insignificant while corrections for Zn and Cu blanks were frequently necessary.

After analysis the separating funnels and test tubes were swilled with MIBK and then washed with distilled water, filled with acid and left overnight for operation the next day. Before use each day all the glassware was washed three times with freshly distilled and deionised water.

Because of the small volume of pore waters available, it was not possible to run replicate analyses in order to check the precision of the method. However, in a sense 4 standard additions can be considered as replicates which enable an estimate to be made of the analytical precision. The analytical precision for the various elements based on 8 separate determinations is given in Chapter 8.

Analysis of trace metals in ultrafiltrate and retentate

The trace metal concentrations in the ultrafiltrate were measured on a 15 mls sample in exactly the same way as the trace metals in the untreated samples. The total volume of retentate available was only 5 - 10 mls and thus it was not possible to use a standard additions method for the analysis of trace metals. An accurately measured volume of retentate, either 5 or 10 mls depending on the volume available, was diluted to a volume of 15 mls with distilled and deionised water. This single 15 mls sample was then analysed in the same manner as the untreated pore waters. The concentrations of trace metals in the retentate were calculated using the results of the trace metal determinations on the ultrafiltrate of the same sample as a calibration curve.

Ultrafiltration of the pore waters

Ultramembrane filtration is a technique for the physical separation of high from low molecular weight dissolved material in an aqueous medium. In this study, pore waters were filtered through DIAFLO UM-2 membrane filters (nominal exclusion limit MW = 1000) in an AMICON ultrafiltration cell.

The cell was set up and the membrane filters activated according to the manufacturers' instructions. A subsample of ~ 100 mls of pore waters was placed in the ultrafiltration cell and a pressure of 50 p.s.i. of nitrogen was applied to the cell. Ultrafiltered pore waters were collected in acid cleaned polythene bottles until such a time as less than 10 mls of the pore waters remained in the cell. The pressure was then released and the retentate placed in an acid cleaned polythene sample bottle. A single filtration took

approximately 6 hours to complete. The weight of the ultrafiltrate and retentate was measured and used in calculations to estimate the partitioning of HMW organics and trace metals in the original untreated pore waters (see Chapter 8.1). Although no experiments were performed in this study to test the efficiency of filtration as claimed by the manufacturers, other workers, Ogura (1974) and Willander (1972) have calibrated these filters and found that the Diaflo UM-2 filters exclude approximately 85% of the organic matter of 1000. Note that all the yellow colour and greater than 95% of the absorbance at 280 nm of the pore waters ultrafiltered in this study were retained behind the membrane filter.

The ultrafiltered pore waters were analysed for trace metals and for DOC by both absorption and dry combustion techniques.

Oxidation of pore waters by UV light in a stream of oxygen

Acidified pore waters were exhaustively oxidised by UV light predominately 365 nm in a stream of oxygen. 75 mls of pore water was acidified to pH = 2 with aristar HCl and transferred to a glass reaction vessel. A 100 Watt medium pressure Hg lamp (APPLIED PHOTOPHYSICS) was placed in a water cooled quartz immersion well which was then placed coaxially in the reaction flask. A slow stream of oxygen was then bubbled through the reaction vessel and the lamp switched on. Oxidation was continued for 20 - 24 hours. The oxidised pore water was then transferred to acid cleaned polythene bottles. The reaction vessel was acid cleaned and rinsed 3 times with distilled water between each sample.

Experiments were performed to examine the kinetics and completeness of oxidation by this process (see Chapter 8). In addition, the

absorption at 280 nm, as a measure of DOC, was measured on every sample and only if the absorption was less than 5% of the untreated value was oxidation considered to be complete. If oxidation was incomplete, the samples were oxidised for a further 24 hours. The oxidised samples were analysed for total phosphorus and also ultra-filtered and analysed for trace metals.

Acid insoluble precipitate

When highly anoxic yellow pore waters are acidified (pH = 2) and stored for more than a few days, a brown flocculant precipitate is formed (Presley et al., 1972; Taylor, 1974; this study). The nature of this precipitate was studied initially to examine whether acidification significantly reduced the concentration of trace metals in the pore waters and then to understand the chemical nature of this precipitate.

A set of pore waters from core A2C were acidified to pH = 2 using aristar 2N HCl and at 5^{o}C for a few weeks. The pore waters were vacuum filtered through a 0.45 μ NUCLEOPORE filter and the precipitate collected. The pH of the filtrate was adjusted to $\sim$ 8 with NaOH and the absorbance at 280 nm measured (Table 6 IV) in order to estimate the fraction of DOC present in this precipitate.

The IR spectrum of the acid insoluble precipitate was measured on a UNICAM S.P. 1200 infrared spectrophotometer. The sample was dried in a dessicator and presented to the spectrophotometer on the nucleopore filter balanced against a similar membrane filter.

The acid insoluble precipitate was also analysed for the major elements Al, Ca, Mg, Fe and P (Table 6 V) by a thin film X-ray fluorescence technique similar to that used for the analysis of suspended

particulate matter (see below).

Analysis of major elements in particulate matter (and in the acid insoluble precipitate)

The chemical analysis of Ca, Fe, Ti, Si, Al, K, Mg and P was undertaken using a thin film X-ray fluorescence technique (PW 1212 spectrometer). The technique is reported in detail in Taylor (1974), including the preparation of standards, presentation of samples and discussion of analytical problems. A less detailed description of the method is given in Price and Calvert (1973) and Skei (1975). Only a summary of the technique is included here.

Standards were prepared by suspending known amounts of various UGS standard rock powders (1 - 5 μg) in distilled water and filtering through Nucleopore membrane filters. The range of standards was such that extrapolation was unnecessary.

Straight line calibration curves were plotted manually for all elements and the appropriate parameters fed into a computer program used to process the data (Edinburgh Regional Computing Centre). No salt correction was applied to those elements which were analysed in the suspended particulate matter. A salt correction was applied to the Ca and Mg analyses from the acid insoluble precipitate. It was assumed that all the K in the sample was due to sea salt and that the K/Ca and K/Mg ratios are the same as those for sea water.

Instrument conditions are given in Skei (1975) and analytical precision from 6 replicates in Table B II.

Sediment mineralogy

The dried, ground sediment powder was pressed into aluminium

sample holders. A PHILIPS X-ray diffractometer (PW 1011/1050) was employed with Ni filtered Cu radiation ($CuK\alpha$). Each sample was scanned (1^{o} per minute) from 4^{o} (2θ) to 40^{o}(2θ).

Major elements in the sediment

The major elements (Fe, Ti, Al, Si and P) were determined by X-ray fluorescence spectrometry employing an analytical method similar to that described by Rose et al. (1963). All the elements were determined using a PHILIPS PW 1212 multi-channel spectrometer.

A mixture of dried sediment, ground in the tungsten carbide disc mill, lanthanum oxide (heavy absorber) and lithium tetraborate (flux and diluent) in the ratio 1:1:8 was fused at $1050^{o}C$ for 20 minutes. When cool, the fused beads were made up to their original weight by further addition of $Li_2B_4O_7$, thus compensating for the loss of volatiles.

The samples were then reground in the TEMA tungsten carbide disc mill for 2 minutes and redried at $110^{o}C$ overnight. Finally the samples were pelletised at 15 tons pressure for 1 minute with boric acid as backing material.

Standards (Table B III) were prepared in an identical manner. The standards and samples were analysed in sets of four, of which one was kept in continually as a monitor to correct for drift in the machine. The data was processed using an interactive computer program set up by R.F. Cheeney (Grant Institute of Geology, Edinburgh). The calibration curve was checked manually if the calculated concentration of the standards differed significantly from the measured standards. The analytical precision (6 replicates of one disc) is

Table B II

Analytical precision of X-ray fluorescence analyses of sediments (Skei 1975)

Element	Analytical precision	Element	Analytical precision
Fe	2%	Cu	4%
Ti	2%	Zn	3%
Si	2%	Pb	5%
Al	2%	Fe	5%
P	10%	Mn	5%
		Rb	6%

Analytical precision of X-ray fluorescence analysis of suspended particulate matter

Fe	1%
Ti	5%
Si	5%
Al	2%
P	4%
Ca	2%
Mg	3%
K	2%

Table B III

Standards used for X-ray fluorescence spectrometry (sediments)

Code	Type of material	Source
	Major element analysis	
E1*	Ferrogabbro	Grant Inst. of Geology Standard
E2*	Basalt	ditto
E3*	Fjord sediment	ditto
98a	Plastic clay	U.S. National Bureau of Standards
G2*	Granite	U.S.G.S. Standards
	Trace element analysis	
GSP1	Granodiorite	U.S.G.S. Standards
DTS1	Dunite	ditto
W1	Diabase	ditto
AGV1	Andesite	ditto
PCC1	Peridotite	ditto
BCR1	Basalt	ditto
BL3571	Amphibolite	Bristol
synthetic standards (see text)		

* Standards used for both major and trace element analysis.

shown in Table B II.

Trace elements in the sediment

Trace elements (Cu, Pb, Zn, Fe, Mn, Rb and I) in the sediments were analysed by X-ray fluorescence spectrometry (PW 1212) using the method of Reynolds (1963). Approximately 4 grams of sediment sample (dried at 110°C and ground in an agate TEMA disc mill) was pelletised. The mass absorption coefficients were estimated by measuring the intensities of the Compton-scattered portion of a $Mo_K\alpha$ primary beam (for instrument conditions see Skei, 1975). Standards (Table B III) of known mass absorption coefficients and samples were run in a similar way to that described for major element analyses.

The spectrometer conditions for the analysis of trace elements are shown in Skei (1975). International standards were used for all the trace metals except for I for which synthetic standards were used. The latter was made up to cover the wide range of I concentrations in the sediments. A dilution series ranging between 40 ppm and 800 ppm was prepared by S. Strain (Grant Institute of Geology) using as a base (E1), a ferrogabbro which had no iodine in it, and AgI. The working curve was linear and retained its gradient and intercept over a number of successive determinations, a correction for matrix differences was made following Reynolds (1963).

The precision of analysis is shown in Table B II.

Chemical treatments of the sediment

Hydrogen peroxide

5 - 10 mls of H_2O_2 (100 vol) was added to 2 - 3.5 grams of dry ground sediment in a conical flask. Sediment samples from core M18

were also acidified with 1 - 2 mls of HCl (Aristar), while the samples from core F1 remained non acidified. The samples were then heated. Reaction was difficult to control and frequently an oxygen rich foam flowed over the top of the flask. A dousing with cold distilled water was used to control the reaction. After approximately an hour the foaming subsides, an excess of H_2O_2 was then added and the flask boiled until no further reaction was visible. The sediment was now light brown to white in colour. The sample was centrifuged, washed and centrifuged again. It was then transferred to a glass jar and dried in the oven at 120°C ready for grinding and analysis.

Sodium pyrophosphate

A solution of O.I.M. sodium pyrophosphate was made up and its pH adjusted to 7 with 2N HCl. 25 mls of pyrophosphate was added to 2.5 - 4 grams of sediment and heated to boiling on a hotplate. The sample was allowed to cool and the brown coloured liquid decanted off. The procedure was repeated with a further 25 mls and then centrifuged, washed with distilled water and centrifuged again. The sediment sample was then transferred to a glass jar and dried in the oven at 120°C.

Sodium dithionite

This chemical treatment is based on that of Mehta and Jackson (1960) for the removal of oxides from clays without destroying the clay lattice. 25 mls of 0.3M sodium citrate and 10 mls of 0.5M sodium bicarbonate were added to 2.5 - 3 gram samples of dry ground sediment. This was heated to 70 - 80°C on a hot plate and 1 gram of sodium dithionite added. The sample was shaken and left to digest

for 15 minutes. A few mls of sodium chloride, a flocculating agent, was added and after 5 minutes the supernatent liquid was decanted off. The procedure was then repeated. The sample was washed and centrifuged and the sediment transferred to a glass jar and dried at 120°C.

All samples after chemical treatment were analysed for trace metals (by XRF) and for carbon and nitrogen.

Carbonate-carbon in the sediment

Carbonate-carbon was determined by acid treatment (HCl) and measurement of the volume of CO_2 evolved using a gas burette. Ferrous sulphate was added to the sample to prevent hydrolysis of any organic matter. The overall precision was determined from 6 replicates and was found to be $\pm$ 4% (Skei, 1975).

Total carbon in the sediment

This was determined in the samples collected in April 1974 by combusting a known weight ($\sim$ 0.1 grm) of dried ground sediment in a LECO (Laboratory Equipment Corporation) induction furnace (model 521-200; fitted with a catalyst furnace (model 507-100) and sulphur and dust traps). The amount of CO_2 evolved was measured with a LECO gas burette (model 572-100). The analytical procedure is fully described in the LECO instruction manual. The accuracy of the instrument was checked at the beginning of each set of readings using LECO steel rings of known carbon content. The overall precision (6 replicate analyses) was $\pm$ 5% (Skei, 1975).

The total carbon (and total nitrogen) of the samples collected in February 1975 was determined using a PERKIN-ELMER 240 elemental analyser. A known weight ($\sim$10 mg) of dried ground sediment was

combusted in a stream of oxygen at 960°C and the CO_2 and N measured by hot wire detectors. (The analytical procedure is fully described in the LECO instruction manual.) The instrument was calibrated daily using acetanalide. Each sample was run in duplicate and if the results differed by more than 10%, then replicate analyses were performed. 4 samples were analysed both by LECO furnace and by the CN analyser and found to be comparable ($\pm$ 5%).

Organic carbon was assumed to be equivalent to the difference between total-C and carbonate-C as measured above.

Total nitrogen in the sediment

Total nitrogen in the sediment collected in February 1975 was analysed using the PERKIN-ELMER 240 elemental analyser, (see above for method). Nitrogen was determined by the micro-Kjeldahl method following McKenzie and Wallace (1954) on the samples collected in April 1974. 0.1 gram of sample was digested for 20 minutes in 1.5 mls H_2SO_4 (conc.) with 1.5 mls K_2SO_4 and $HgSO_4$ as catalyst. The digest is transferred to a distillation apparatus, 10 mls of NaOH-$Na_2S_2O_3$ solution added and is steam distilled in a weak boric acid solution, which is then titrated against standard potassium hydrogen iodate solution (approx. 0.01N), using a methyl red - methylene blue indicator, until the lilac end point is reached. A batch of six samples can be analysed in 5 hours by this method. Yields of 95 - 103% were obtained using DL α - alanine. The precision is $\pm$ 2% (Doff, 1969).

Replicates of total nitrogen analysed by both methods were comparable ($\pm$ 5%).

Correction of chemical analysis for the effect of sea salt

Samples of dried marine sediments are composed of two fractions - the sediment fraction and the salt fraction. The dilution effect of this salt fraction on the major and minor element analyses was corrected for by measuring the loss in weight on drying the untreated sediment and assuming a normal salinity for the pore waters. The correction applied for this salt effect was usually 10%.

$$\% \text{ salt in dry sample} = \frac{3.5W}{100 - 0.965W}$$

Where W = Water content of the original sample

i.e. $\frac{\text{Dry weight}}{\text{Total weight}} \times 100\%$

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